

Organic semiconducting material and use thereof in organic devices

Field of the invention

The invention relates to an organic material of the formula I and to the use thereof in semiconducting components.

5 Prior art

Organic electronics use interconnections of electrically conductive polymers or small organic molecules. Organic-electronic components in this context may be, for example, displays, data memories or transistors, including field-effect transistors in particular. These
10 components also comprise organic-optoelectronic components, examples being organic photoactive components such as solar cells and photodetectors, which comprise a photoactive layer in which incident radiation generates charge carriers, e.g., bound electron-hole pairs (excitons). Further optoelectronic components are light-emitting
15 electroluminescent components, which emit light when a current flows through them. Optoelectronic components comprise at least two electrodes, with one electrode being applied on a substrate and the other acting as a counterelectrode. Located between the electrodes is at least one photoactive layer, preferably an organic photoactive
20 layer. Further layers, transport layers for example, may be disposed between the electrodes.

Through the use of suitable innovative organic materials it is possible to provide a variety of innovative components. There is therefore development of new applications which are thin, flexible,
25 lightweight, and also have color variability and in addition are inexpensive.

Technical problem

There continues to be a search for organic semiconducting materials which when used in organic electronic components result in an
30 improvement in the properties of the components.

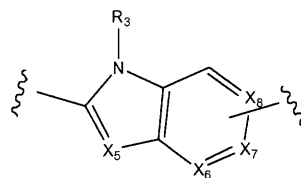
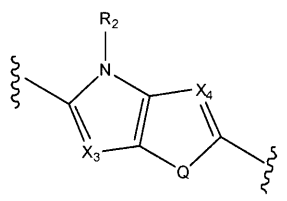
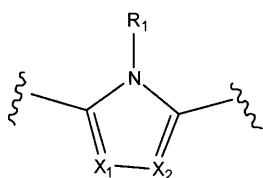
Technical solution

In accordance with the invention this problem is solved by the compounds of the general formula I as claimed in claim 1. Further advantageous embodiments of the compounds, and also advantageous uses

5 EWG1 - (T1)_a - (T2)_b - (Z)_c - (T3)_d - (T4)_e - EWG2

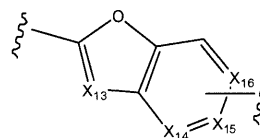
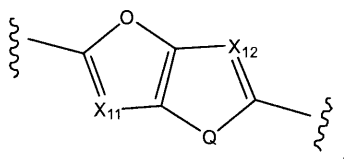
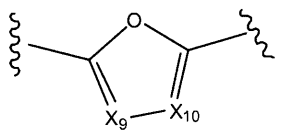
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Formula 3



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Formula 6



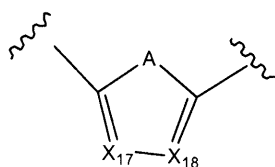
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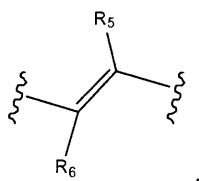
designates the attachment $\sim$ to the other groups in the compound of the general formula I,

- with each R independently of any other being selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, where the substituent may in particular be halogen, e.g., F, and C atoms of the C₁-C₂₀ alkyl may be replaced by heteroatoms, such as O or S; C₂-C₂₀ alkenyl, O-alkyl, S-alkyl, O-alkenyl, S-alkenyl, alkynyl, aryl, heteroaryl, it being possible for hydrogen atoms to be substituted in all of these groups (substituted O-alkyl groups preferred); CN, NR'R'', with R' and R'' each independently of one another being selected from: H, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, e.g., by halogen, and C atoms of the C₁-C₂₀ alkyl may be replaced by heteroatoms, e.g., O or S,
- where R₁, R₂, R₃ each independently of one another are selected from a group composed of H, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, preferably by halogen, and C atoms of the C₁-C₂₀ alkyl may be replaced by heteroatoms, e.g., O or S; substituted or unsubstituted C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, CN,
- with each Q independently of any other being selected from S, O, Se, NR''', where R''' is defined as for R₁ to R₃,
- where the electron-withdrawing groups EWG1 and EWG2 independently of one another are electron-withdrawing groups having at least one C=C double bond,
- where the groups T1, T2, T3 and T4 each independently of one another are selected from:

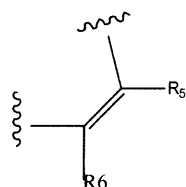
Formula 10



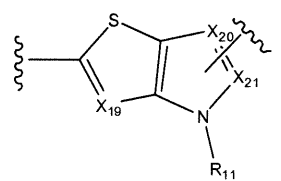
Formula 11



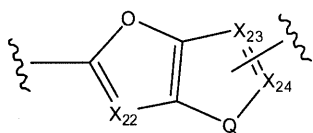
Formula 11*



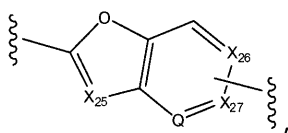
Formula 12



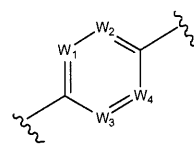
Formula 13



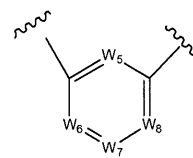
Formula 14



Formula 15



Formula 16

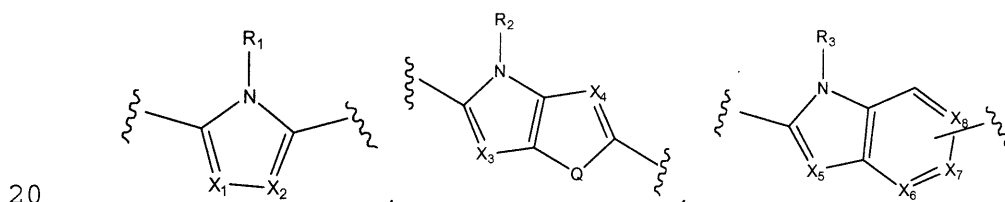


- and $\sim$ designates the attachment to the other groups in the compound of the general formula I,
- 5 - with R_5 and R_6 each independently of one another being selected from a group: H, CN, F, aryl, heteroaryl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, where hydrogen atoms of the C_1 - C_{20} alkyl may be substituted, e.g., by halogen, where, if the substituent R_{13} is present in
- 10 the compound of the formula I, a ring closure between R_5 with R_{13} or R_6 with R_{13} is possible, with the proviso that between R_5 and R_{13} or between R_6 and R_{13} in each case the double bond from formula 11 or 11* is located, is possible,
- with W_1 to W_8 each independently of one another being selected
- 15 from N, CR, where R is defined as described above,
- with X_{17} to X_{27} independently of one another being selected from C-R, where R is defined as described above, and with the proviso that in the groups of the formulae 12, 13 and 14, in each case one group from the groups X_{20}/X_{21} , X_{23}/X_{24} and X_{26}/X_{27} designates
- 20 the attachment $\sim$ to the other groups in the compound of the general formula I,
- with A being S, O, NR''''', Se
- with Q being S, O, NR''''', Se
- where for the groups A and Q, the substituent R''''' in each case
- 25 independently of any other is selected from H, CN, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, where the H atoms of the C_1 - C_{20} alkyl may be substituted, where there may in particular be substitution by halogen, e.g., F; C_2 - C_{20} alkenyl, O-alkyl, S-alkyl, O-alkenyl, S-alkenyl, alkynyl, substituted or
- 30 unsubstituted aryl, substituted or unsubstituted heteroaryl.

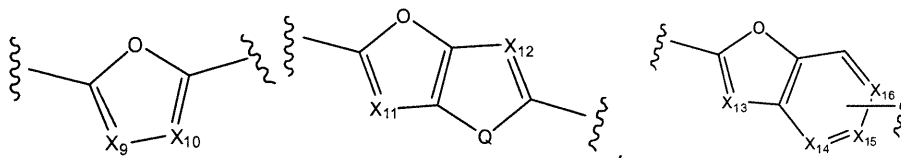
Surprisingly it has been ascertained that in the case of the compounds of the invention, by the common structural element in the donor block Z, that at least one group M and one group N are each linked in such a way that at least one N atom of the group M and one O atom of the group N are joined to one another in each case via 2 C atoms, these compounds broadly and strongly absorb radiation, especially light, something which is able to lead to elevated efficiencies in organic photoactive components. Moreover, these compounds also have an enhanced charge carrier mobility, and so organic electronic components, such as transistors, which comprise the compounds of the invention are also able to exhibit improved electrical values.

The compounds of the invention may in particular also be used as charge carrier transport layers, e.g., p-conducting materials. The absorption spectrum and emission spectrum may extend starting from the lower UV through to the infrared spectral range.

The above-described at least one group M is selected from pyrrole structures or fused pyrrole scaffolds with at least one N atom, of the following general formulae 1 to 3:



This group M is joined directly to at least one group N which is selected from furan structures or fused furan scaffolds having at least one O atom, of the following general formulae 3 to 5:



25 It is possible here that in the middle group Z there may also be a succession of a plurality of dual groups composed of M-N and/or N-M blocks if the parameter c is > 1, e.g., *-M-N-M-N-M-N-*, *-M-N-N-M-M-N-N-*, or *-N-M-N-M-N-M-N-M-*,

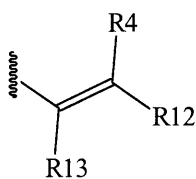
On the basis of this structural feature $(\text{*}-\text{M}-\text{N}-\text{*})_c$ or $(\text{*}-\text{N}-\text{M}-\text{*})_c$, the present compounds have a high optical density, preferably in the visible spectral range, and in particular a high integral over the optical density in the absorption spectrum in comparison to compounds
 5 not of the invention which do not have the above-described structural element. "Integral" here means the area content below a curve in the absorption spectrum, which is an important feature for the suitability of the material as an organic photosensitive material.

The present compounds of the invention of the general formula I may,
 10 in addition to the electron donor group Z which is always present, have further electron donor groups T1, T2, T3 and T4, which result in a further extension of the conjugated π -electron system already present through Z. The electron donor groups are flanked by terminal electron acceptor groups EWG1 and EWG2.

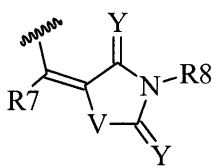
15 The compounds of the invention are, in particular, what are called "small molecules", by which are meant nonpolymeric, oligomeric, organic molecules having a molar mass between 100 to 2000 g/mol, which in particular may also be monodisperse.

The electron-withdrawing groups EWG1 and EWG2 may preferably
 20 independently of one another be selected from:

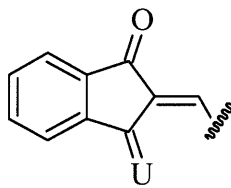
Formula 7



Formula 8



Formula 9



- and $\sim$ designates the attachment to the groups T1 to T4 or Z in the compound of the general formula I,

25 - with R_4 and R_{12} each independently of one another being selected from H, CN, COOR, with the proviso that R_4 and R_{12} cannot both be H,

- where R is selected from the same group of compounds as defined in the case of R_1 to R_3 ,

30 - with each R_{13} independently of any other being selected from a group: H, CN, F, aryl, heteroaryl, C_2 - C_{20} alkenyl, alkynyl,

branched or linear, cyclic or open-chain C_1-C_{20} alkyl, where hydrogen atoms of the C_1-C_{20} alkyl may be substituted, where, if the substituent R_5 or R_6 is present in the compound of the formula I, a ring closure between R_5 with R_{13} or R_6 with R_{13} is possible, with the proviso that the double bond from formula 11 or formula 11* is located in each case between R_5 and R_{13} or between R_6 and R_{13} ,

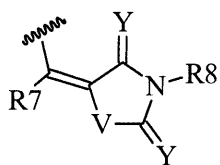
- with V being O, S

- with Y being O, S, $C(CN)_2$

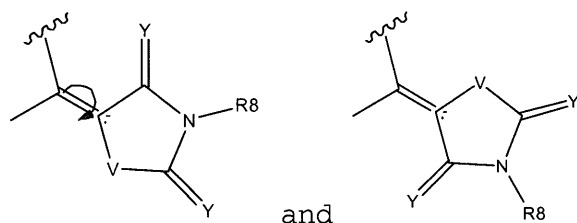
10 - with U being O, S, $C(CN)_2$

- with R_7 and R_8 each independently of one another being selected from a group H, CN, F, aryl, heteroaryl, C_2-C_{20} alkenyl, alkynyl, branched or linear, cyclic or open-chain C_1-C_{20} alkyl, where hydrogen atoms of the C_1-C_{20} alkyl may be substituted, where for each of the groups EWG1 and EWG2, each independently of one another in each case for each C=C double bond, both the E-isomer and the Z-isomer may be present.

For each C=C double bond in the formulae 7, 8 and 9, therefore, both the E-isomer ("E" = German entgegen = contrary; i.e., trans configuration) and the Z-isomer ("Z" = German zusammen = together; i.e., cis configuration) may be present, these isomers being formed by an imaginary rotation by 180° about the axis of the C=C double bond. This will be explained below using as example the radical of the formula 8:



Both isomers, which may be present separately from one another, can be converted into one another by an imaginary rotation about the C=C double bond (indicated by the arrow on the double bond), thus resulting in the following two isomers for the group of the formula 8:



Furthermore, in particular, EWG1 may be the same as EWG2.

5 In the compounds of the invention of the general formula I, the aryl groups and the heteroaryl groups may preferably be C₅-C₁₀ aryl and C₅-C₁₀ heteroaryl groups. Substituents are understood to be all atoms and groups of atoms other than hydrogen. Substituents contemplated include, in particular, halogen, e.g., fluorine, or else C₁-C₅ alkyl
10 groups, which may be substituted in turn. The O-alkyl, S-alkyl, O-alkenyl, S-alkenyl and alkynyl groups may each be C₁-C₂₀ groups, preferably C₁-C₅ groups.

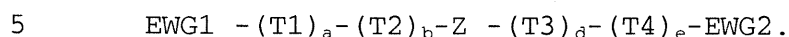
The cyclic or open-chain C₁-C₂₀ alkyl groups of the compounds of the formula I of the invention may be linear or else branched and are
15 preferably C₁-C₅ alkyl groups. Nonadjacent and nonterminal C atoms in these alkyl groups may be replaced by heteroatoms.

By "heteroatoms" in the sense of the present compounds of the formula I are meant, in particular, O, S, Se or NR''''', with the substituent R''''' being defined like the substituents R₁ to R₃ which have already
20 been described above.

The bonding locations for the individual groups, which are designated by ξ , characterize the points of attachment of the respective groups to the other groups of the compounds of the formula I; in other words, for example, for the electron-withdrawing group EWG1 in the
25 compound of the formula I, the attachment either to the donor groups T1 (for a = 1) or T2 (for a = 0 and b = 1), or to the donor group Z if the parameters a and b are both 0.

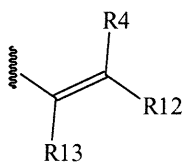
These organic materials are applied in the form of thin films or in small volume to the foils by printing, bonding, coating, vapor
30 deposition or otherwise. Methods contemplated for the production of

the thin layers are also all those which are also used for electronics on glass, ceramic supports or semiconducting supports. According to a further embodiment of the present invention, in the compounds of the formula I $c = 1$ with the general formula



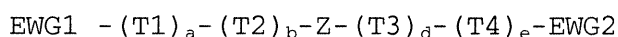
The inventors have ascertained that one donor block Z is sufficient to obtain an increased optical density relative to structurally different compounds.

Furthermore, the electron-withdrawing groups EWG1 and EWG2 may
10 independently of one another be the following groups of the formula 7:

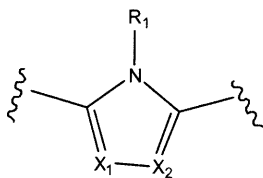


Electron-withdrawing groups EWG1 and EWG2 of this kind lead to oligomeric compounds of the formula I which can be applied
15 particularly effectively by vapor deposition to substrates. With particular preference, R_4 and R_{12} are CN, thus resulting in the particularly strongly electron-withdrawing group dicyano-vinylene. Moreover, the substituent R_{13} may preferably be H.

According to a further embodiment of the present invention, the
20 compounds of the formula I with $c=1$ of the general formula



with $\text{Z} = \text{*}-\text{M}-\text{N}-\text{*}$ or $\text{*}-\text{N}-\text{M}-\text{*}$ have a group M of the formula 1:



These simple pyrrole structural units for the donor block M, which
25 have no further fused aromatic π -electron system, already lead to a marked increase in the absorption of radiation for the compounds of the invention when they also have the donor group N as well. It is, however, also possible to use fused ring systems as donor block M

which contain pyrrole, such as indoles or other compounds covered by the general formulae 2 or 3, for example.

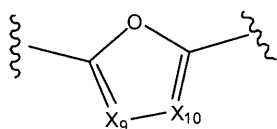
The terms "substituted" and "substituent" should be interpreted in the sense of the present invention to mean that one or more H atoms
 5 have been exchanged for any other group of atoms or another atom.

"Substituents" in this sense may in particular be a halogen or a pseudo halogen, e.g., fluorine or CN, and also an aryl group, e.g., phenyl, or an alkyl group, e.g., a C₁-C₆ alkyl group.

The general groups and substituents in this donor block M of the
 10 general formula I may be defined as follows:

- X₁ and X₂ independently of one another are selected from C-R with each R independently of any other selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl.

15 The further donor block N in structural fragment Z may be the following general group of the formula 4:



These simple furan structural units for the donor block N, which have no further fused aromatic π -electron system, already lead to a marked
 20 increase in the absorption of radiation for the compounds of the invention when they also have the donor group M as well. Also possible, however, is the use of fused donor blocks which receive furan, such as, for example, benzofurans or other compounds covered by the general formulae 5 or 6.

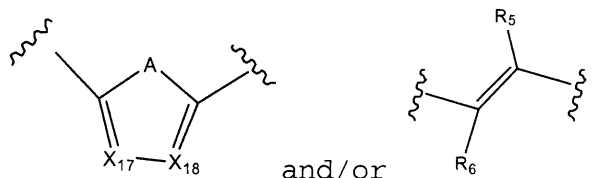
25 The general groups X₉ and X₁₀ in the formula 4 may preferably be selected, independently of one another, from C-R with each R independently of any other being selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl.

The conjugated π -electron system of the donor region of the compounds
 30 of the invention of the formula I may be expanded beyond the donor block Z by incorporation of at least one further donor block T₁, T₂, T₃ or T₄ and correspondingly by setting the parameters a, b, d or e

associated with these donor blocks in the formula I successively to 1.

In particular, a may be 1, and in that case the group T1 may preferably be selected from the groups of the formulae 10 and/or 11:

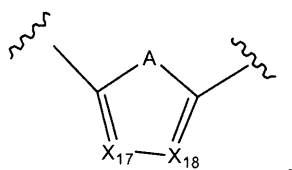
5 Formula 10 Formula 11



For the formula 10, the following in particular may apply: A = S or O.

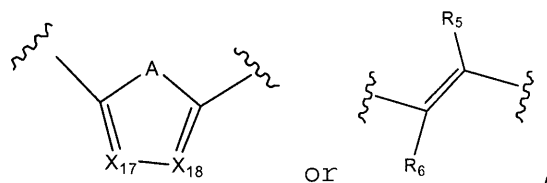
Furthermore, in formula 10, X₁₇ and X₁₈ may be C-R, where R
 10 independently at each occurrence is selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl; R₅ and R₆ each independently of one another are selected from H, CN, F, aryl, heteroaryl, C₂-C₂₀ alkenyl, alkynyl, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl
 15 may be substituted, where, if the substituent R₅ and R₆ is present in the compound, a ring closure between R₅ with R₁₃ and between R₆ with R₁₃ is possible, with the proviso that the double bond from formula 11 or formula 11* is located between R₅ and R₁₃ or between R₆ and R₁₃.

If the donor block T2 is present, b is 1, and T2 is preferably the
 20 general group of the formula 10



In the formula 10, preferably A is S or O. Moreover, in the formula 10, X₁₇ and X₁₈ may be C-R, where R independently at each occurrence is selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl.
 25

When the donor block T3 is present, d is 1, and the group T3 is preferably selected from the groups of the formulae 10 or 11:



where for the formula 10 the following may be the case: A = S or O.

In the formula 10, in particular, X₁₇ and X₁₈ may be C-R, where R independently at each occurrence is selected from a group composed of
 5 H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, R₅ and R₆ each independently of one another are selected from H, CN, F, aryl, heteroaryl, C₂-C₂₀ alkenyl, alkynyl, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, where, if the substituent R₅ and R₆ is present in
 10 the compound, a ring closure between R₅ with R₁₃ or R₆ with R₁₃ is possible, with the proviso that the double bond from formula 11 or formula 11* is located between R₅ and R₁₃ or between R₆ and R₁₃.

Analogously to T3, T4 with e = 1 may also preferably be selected from the groups of the formulae 10 or 11, in which case the general groups
 15 and substituents for these formulae are preferably selected exactly the same as for T3.

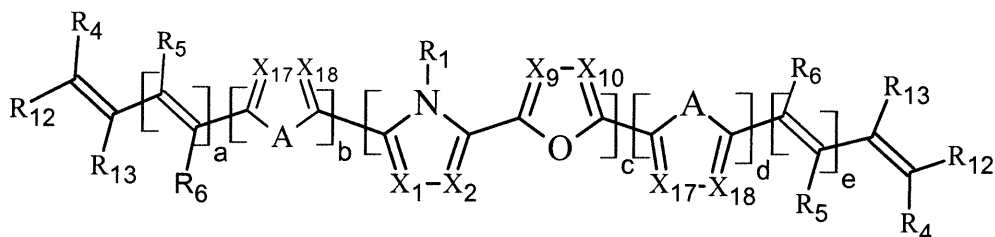
The inventors have ascertained that through the presence in particular of a further heterocyclic group, which may be a furan or a thiophene residue, and also of double bonds which are preferably
 20 located adjacent to at least one of the electron-withdrawing groups EWG1 and/or EWG2, but may also be located between a heterocyclic group and the central donor block Z, it is possible to prepare further molecules of the invention which possess the advantageous properties already stated.

25 Furthermore, the double bonds (formula 11 or formula 11*) may also be present adjacent to both electron-withdrawing groups EWG1 and EWG2.

Also possible is a ring closure between the group R₅ of the formula 11 or formula 11* with the group R₁₃ of the formula 7 of the electron-withdrawing groups EWG1 and/or EWG2, or else between the group R₆ of
 30 the formula 11 or formula 11* with R₁₃ of the formula 7, with the proviso that the double bond from formula 11 is located between R₅ and R₁₃ or between R₆ and R₁₃, with the ring closure being present in particular in the form of an optionally substituted cyclopentenyl

ring or of an optionally substituted cyclohexenyl ring (see, for example, the inventive compounds 1 and 2 in table 1).

In a further embodiment of the present invention, the compounds of the invention have particular preferred donor blocks for the groups Z and T1 to T4, so resulting in a general structural formula II:



The substituents and general groups here may be defined in the manner described already. Preference here is given to the following definitions for the formula II, although in a most general form the definitions valid for the substituents and the general groups are those defined for the compounds of the formula I:

- A is O or S,
- independently of one another X_{17} , X_{18} , X_1 , X_2 , X_9 and X_{10} are C-R, where R independently at each occurrence is selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, R_5 and R_6 each independently of one another are selected from H, CN, F, aryl, heteroaryl, C_2 - C_{20} alkenyl, alkynyl, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, where hydrogen atoms of the C_1 - C_{20} alkyl may be substituted, and where, if the substituents R_5 and R_6 are present, they may form a ring closure between R_5 with R_{13} or R_6 with R_{13} ,
- at least one of the parameters a, b, d or e is 1, and it is also possible for all of these parameters to be 1; preferably at least one of the parameters is 0, e.g., T4, while all other parameters are 1,
- R_4 and R_{12} each independently of one another are selected from H and CN, with the proviso that R_4 and R_{12} cannot both be H.

In a further aspect of the present invention, all of the compounds of the invention described above can be used in an organic electronic component.

In view of the particularly strong absorption of the compounds of the invention, excitons are formed to particularly good effect in layers which comprise these compounds, thus leading, in organic photoactive components comprising these compounds, to higher fill factors FF, improved open-circuit voltage V_{oc} , and improved short-circuit current density J_{sc} . With other organic electronic devices, better electronic values are likewise to be expected in view of the elevated charge carrier transport properties of the compounds of the invention.

The term "organic electronic component" refers to all electronic components which can be produced using organic conducting or semiconducting materials, examples being transistors, such as organic field-effect transistors, organic light-emitting components, organic photoactive devices in which excitons (electron-hole pairs) can be formed in a photoactive layer by irradiation, such as photodetectors, for example, or organic solar cells.

These organic electronic components generally have an electrode and a counterelectrode, with an organic functional layer arranged between them. This organic functional layer may exert a function important for the electronic operation of the organic component, such as a charge carrier transport function, such as the transport of holes (p-conducting) or the transport of electrons (n-conducting).

Furthermore, the organic functional layer may also comprise a light-emitting layer which emits radiation, light for example, when a voltage is applied to the electrode and counterelectrode, through recombination of the holes (positive charges) and electrons (negative charge). The organic functional layer may also be a photoactive layer in which excitons (electron-hole pairs) are formed on irradiation with a form of radiation, light for example, or else UV radiation or IR radiation. With organic photoactive layers, what are called planar heterojunctions may be formed, in particular, in which a planar, p-conducting layer is adjacent to a planar, n-conducting layer and the excitons formed by irradiation either in the p-conducting or the n-conducting layer can be separated into holes and electrons at the interface between the two layers. Furthermore,

the photoactive layer may also comprise what is called a bulk heterojunction, where p-conducting and n-conducting materials transition into one another in the form of an interpenetrating network, where again the separation of the excitons formed by irradiation occurs at the interfaces between p-conducting and n-conducting materials.

Excitons are electrically neutral excitation states, the electron-hole pairs, which are then separated into electrons and holes in a further step at a p-n junction. Separation takes place accordingly into free charge carriers, which contribute to electrical current flow. A limiting factor here is the size of the bandgap of the semiconductor; accordingly, the only photons which can be absorbed are those having an energy which is greater than its bandgap. Light always only generates excitons, not free charge carriers, and hence the low-recombination diffusion is an important component for the level of the photocurrent. The exciton diffusion length here must exceed the typical depth of penetration of the light, so that as large a portion of the light as possible can be utilized electrically.

A construction already known from the literature for a common organic solar cell is composed of a pin or nip diode [Martin Pfeiffer, "Controlled doping of organic vacuum deposited dye layers: basics and applications", PhD thesis TU Dresden, 1999 and WO2011/161108A1]: a pin solar cell consists of a carrier/substrate followed by a usually transparent base contact, p-layer(s), i-layer(s), n-layer(s), and a top contact. A nip solar cell consists of a carrier/substrate followed by a usually transparent base contact, n-layer(s), i-layer(s), p-layer(s) and a top contact.

Here, n and p doping, respectively, mean doping leading to an increase in the density of free electrons and holes, respectively, in the thermal equilibrium state. Such layers are therefore to be understood primarily as transport layers. It is also possible for n- or p-layer(s) to be at least partly nominally undoped and to possess preferably n-conducting or p-conducting properties solely on the basis of the physical properties (e.g., different mobility) or on the basis of different impurities (e.g., residues from the synthesis or from layer production) or as a result of environment effects (e.g.,

bordering layers, inward diffusion of metals or other organic materials, gas doping from the surrounding atmosphere). In this sense, such layers should be understood preferably as transport layers.

- 5 The excitons pass by diffusion to an interface of this kind where electrons and holes are separated from one another. The material which accepts the electrons is referred to as the acceptor, and the material which accepts the holes is referred to as the donor.

The designation "i-layer" marks out an undoped or intrinsic layer.

- 10 One or more i-layers here may consist of one material (planar heterojunctions) or else of a mixture of two or more materials, referred to as bulk heterojunctions, which have an interpenetrating network.

- Also known from the literature are organic pin tandem cells and pin
15 multiple cells (DE 10 2004 014 046). WO 2011 161 108 A1 discloses in this regard a proposal for realization in the form of a photoactive component having an electrode and a counterelectrode, there being at least one organic layer system arranged between the electrodes, and also having at least two photoactive layer systems and, between the
20 photoactive layer systems, at least two different transport layer systems of the same charge carrier type, characterized in that a transport layer system is adapted energetically to one of the two photoactive layer systems and the other transport layer system is implemented transparently.

- 25 The organic electronic components may also comprise further metal oxide layers.

Aspects of the present invention are elucidated in more detail additionally below, using figures and exemplary embodiments. In the figures

- 30 figures 1 to 3 show the absorption spectra of inventive compounds in comparison to unclaimed compounds;

figures 4 to 6 show current-voltage curves of organic photoactive components (solar cells) which comprise inventive compounds;

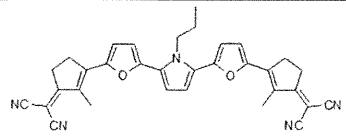
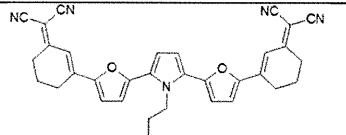
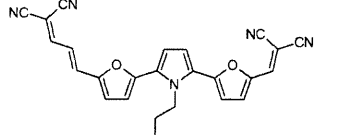
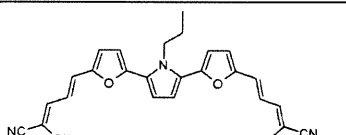
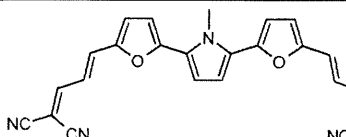
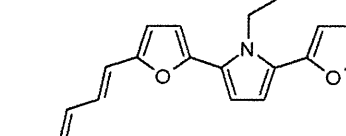
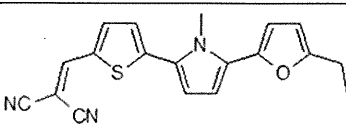
- figure 7 shows an exemplary organic photoactive component in cross
35 section;

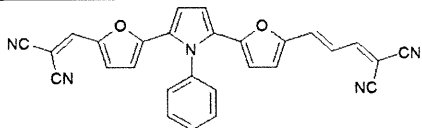
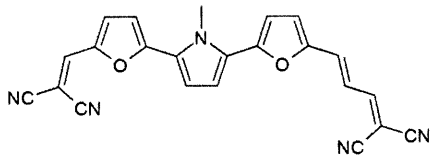
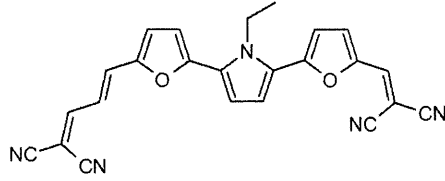
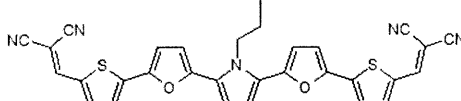
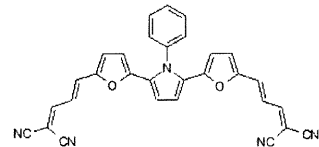
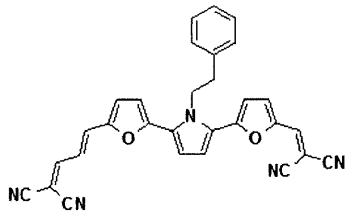
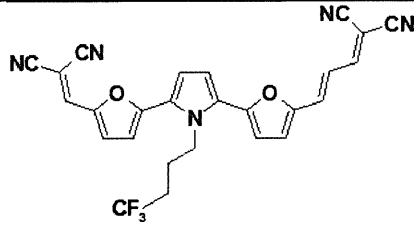
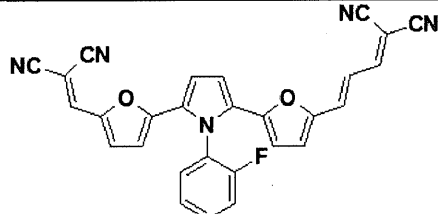
figure 8 shows an overview of the synthesis of inventive compounds.

Table 1, in an overview, shows the structures, melting points, and absorption maximum (in nm and eV in the solvent (SV)) of exemplary embodiments of inventive compounds covered by both the general

5 formulae I and II. The synthesis of these compounds is elucidated in detail additionally later on below.

Table 1:

Number	Structure	M.p./°C ^a	λ_{max} (SV)/nm ^b	λ_{max} (SV)/eV ^b
1		290	528	2.35
2		292	544	2.28
3		224	555	2.23
4		261	590	2.10
5		231	575	2.16
6		263	596	2.08
7		265	543	2.28

Number	Structure	M.p. / °C ^a	λ_{max} (SV) / nm ^b	λ_{max} (SV) / eV ^b
8		254	566	2.19
9		246	553	2.24
10		245	568	2.18
11		243	542	2.28
12		279	596	2.09
13		206	550	2.26
14		212	547	2.27
15		255	543	2.29

Number	Structure	M.p. / °C ^a	λ_{max} (SV) / nm ^b	λ_{max} (SV) / eV ^b
16		292	568	2.19
17		264	543	2.29
18		270	595	2.09
19		199	543	2.29
20		not det.	not det.	not det.
21		not det.	not det.	not det.
22		279	529	2.35

^a Onset DSC (differential scanning calorimetry; start of melting range; extrapolated initial temperature (intersection of inflection tangent and baseline))

^b In dichloromethane unless otherwise noted

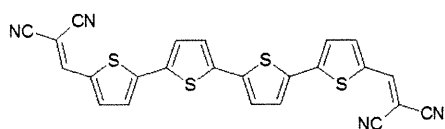
Surprisingly it has been found that the inventive compounds exhibit particularly strong absorption (i.e., high optical density at the absorption maximum or high integral over the optical density in the

visible spectral range in comparison to similar compounds outside the range claimed here).

In this context, figure 1 shows a comparison of the absorption spectra (optical density over wavelength in nm) for vacuum-deposited films 30 nm thick, for the inventive compounds 4 and 10 of table 1 in comparison to two noninventive compounds: comparative material 1 and comparative material 2.

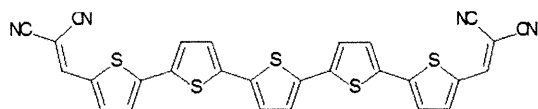
The structures and scientific publications relating to the syntheses of the two comparative materials are as follows:

10 Comparative material **1**:



(Fitzner et al., Adv. Funct. Mat. 2011, 21, 897-910)

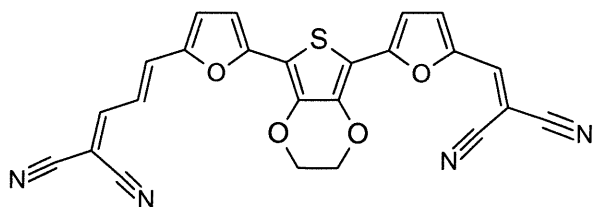
Comparative material **2**:



15 (Fitzner et al., Adv. Funct. Mat. 2011, 21, 897-910).

From the absorption spectra of figure 1 it can be seen that the inventive compounds absorb radiation to a substantially greater extent than the comparative compounds, and therefore have a higher optical integral over the optical density in the visible spectral range.

The advantageous synergistic effect of inventive compounds which comprise EWG1 and EWG2 groups in interaction with a donor block comprising a furan unit directly alongside a pyrrole unit is also apparent from the following, very direct comparison of the inventive compounds 7, 9 and 10 of table 1 with the comparative compound **3** having the following structure:



which contains an EDOT group instead of pyrrole.

Table 2 below shows various parameters of this series of materials in direct comparison. The photovoltaic parameters V_{oc} , J_{sc} and FF relate
 5 in each case to solar cells with a mixed layer, 30 nm thick, of the respective donor material of these compounds and fullerene C60 as photoactive layer on glass, with a construction of ITO / C60 (15 nm) / the respective compounds: C60 (30 nm) / BPAPF (10 nm) / BPAPF:NDP9 (30 nm) / NDP9 (1 nm) / Au (50 nm), measured under AM1.5
 10 illumination (A_m = Air Mass; AM = 1.5 for this spectrum amounts to the overall radiant power 1000 W/m²; AM = 1.5 as standard value for the measurement of solar modules). ITO here serves as an anode, and the adjacent fullerene C60 serves as an electron transport layer ETL, being followed by the photoactive layer as bulk heterojunction
 15 between C60 as electron acceptor material and the respective compound as hole acceptor material (donor material), followed by BPAPF (9,9-bis[4-(N,N-bis-biphenyl-4-yl-amino)phenyl]-9H-fluorene) as hole transport layer HTL and by BPAPF doped with NDP9 (Novaled AG), followed by an Au cathode.

20 The spectral data of figure 2 show the absorption spectra of comparative material 3 in comparison with inventive compounds 7, 9 and 10. The data relate to layers 30 nm thick applied by vacuum deposition to fused silica, and show that the inventive compounds have a higher optical integral over the optical density in the
 25 visible spectral range than noninventive compounds of similar structure.

Table 2 shows the optical density at the absorption maximum (OD_{max}), the optical integral in the visible range (OD-integral), and also V_{oc} , J_{sc} , FF, and the efficiency:

Substance	OD_{max}	OD-integral (400-900 nm) [nm]	V_{oc} [V]	J_{sc} [mA/cm²]	FF [%]	eff [%]
Compound 10 (values in parentheses for cell with optimally adapted hole transport material)	0.45	111 / 237	0.91 (0.91)	14.6 (14.9)	70.8 (73.4)	9.4 (10.0)
Compound 9	0.53	130 / 242	0.91	13.2	71.3	8.6
Compound 7	0.44	105 / 232	0.94	11.7	59.3	6.5
Comparative compound 3	0.35	88 / 307	0.91	11.5	59.1	6.2

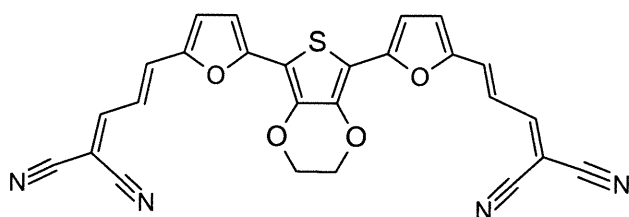
Independently of the substituent, compound 10 exhibits not only higher absorption maxima but also a significantly greater integral absorption in the visible range, although the donor strengths of pyrrole and EDOT are very similar. The superior properties of the inventive substances (compounds 9 and 10) in comparison to comparative material 3 are evident also, with an identical solar cell construction, in the photovoltaic parameters of fill factor (70%-73% for compounds 9 and 10 versus 59% for comparative material 3 with in each case photoactive layers 30 nm thick) and photocurrent J_{sc} (13.2 - 14.9 mA/cm² for compounds 9 and 10 versus 11.5 mA/cm² for comparative compound 3). The significantly increased FF suggests that the compounds 9 and 10 have not only improved absorption properties but also superior charge carrier transport properties. Impressive evidence of the unusual transport properties of the class of substance claimed in accordance with the invention is the very high fill factor of 73% found for compound 10, despite the fact that compound 10 is a very short oligomer which comprises one double bond less than comparative material 1 and three double bonds less than comparative material 2.

Even the inventive compound 7 is still on an advantageous trend relative to the comparative compound 3, despite the significant drop

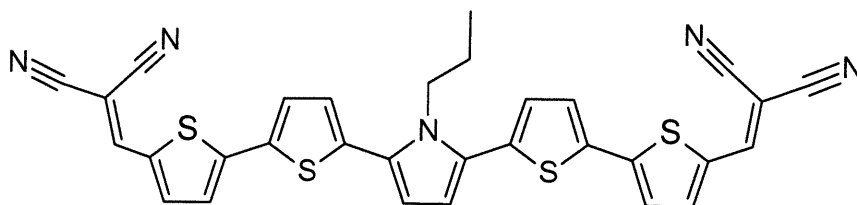
it suffers as a result of the steric hindrance in direct vicinity between thiophene and pyrrole relative to the optimized compounds 9 and 10 (with furan on both sides of the pyrrole).

In a similar way, the advantages of the inventive substances are apparent in a further series of directly comparable, in this case mirror-symmetrical materials, which each have in common certain structural elements with the inventive compound 4 of table 1:

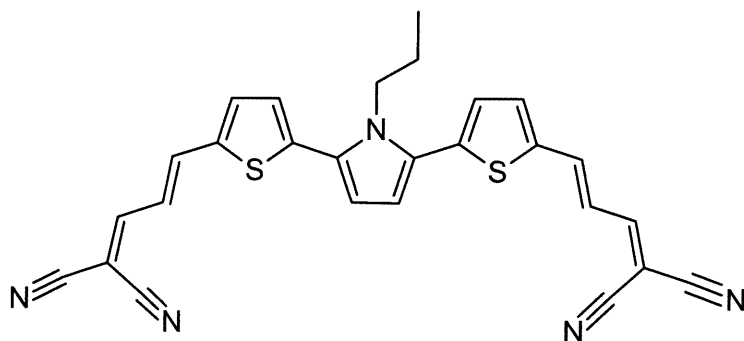
Comparative material 4:



10 Comparative material 5:



Comparative material 6:



15 The absorption spectra of the materials are shown in figure 3. The spectral data relate to layers 30 nm thick applied by vacuum deposition to fused silica.

Table 3 below shows various parameters of this series of materials in direct comparison. The photovoltaic parameters V_{oc} , J_{sc} and FF relate in each case to solar cells having a mixed layer 30 nm thick and composed of the respective donor material and fullerene C60 as photoactive layer on glass, with a construction of ITO / C60(15 nm) /

corresponding compound: C60 (30 nm) / HTM81 (10 nm) / HTM81:NDP9 (30 nm) / NDP9 (1 nm) / Au (50 nm), measured under AM1.5 illumination. The spectral data are based on layers 30 nm thick applied by vacuum deposition to fused silica.

5 Table 3:

Substance	OD _{max}	OD-integral (400-900 nm) [nm]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	eff [%]
Compound 4	0.53	156	0.81	13.3	67.4	7.3
Compound 6	0.4*	114*	0.81	15.1	69.7	8.5
Comparative material 4	0.45	134	0.82	12.3	66.5	6.7
Comparative material 5	0.37	91	0.88	10.4	57.4	5.3
Comparative material 6	0.52	127	0.9	10.4	43.1	4.0

* Compound 6 exhibits severe tendency toward crystallization, thereby clouding the strong absorption in pure layers on glass. Mixed layers with fullerene C60 are less rough and display the expected strong absorption, which is manifested in the unusually high J_{sc}

10 value for the solar cell based on the mixed layer.

Table 3 shows first of all that none of the comparative substances has an absorption integral at a similarly high level as compound 4. The closest in this connection is the closely structurally related comparative compound 6; the latter, however, has a much narrower and less structured spectrum, a fact probably attributable to a lower tendency toward self-organization, i.e., less-ordered layers (steric hindrance between pyrrole and thiophene), a phenomenon manifested drastically in the very much lower fill factor of the solar cell.

20 Similar comments also apply to comparative compound 5, which, however, displays very much weaker absorption. Comparative material 4 with EDOT in place of the inventive pyrrole unit also drops off

significantly in key parameters relative to compound 4 - similarly, as shown above, to comparative material 3 in relation to compound 10.

It has also been possible to show that numerous derivatives of the inventive compounds are able not only to absorb light but also to be vacuum vapor-deposited without residue, whereas, for example, the comparative compound 6 shown above (with thiophene instead of furan as in compound 4) has a large decomposed residue in the vaporizer source.

Through very good charge transport properties and good absorption properties (see above) it is possible to generate high photocurrents with excellent fill factors. Accordingly it is possible to produce very well-combined tandem/triple/quadruple or multiple junction solar cells.

Figure 4 shows the current-voltage curve with a BHJ cell having the following construction: ITO / C60 (15 nm) / compound **4**:C60 (20/30 nm, 1:1, 70°C) / BPAPF (10 nm) / BPAPF:NDP9 (30 nm, 9.1%wt) / NDP9 (1 nm) / Au (50 nm), the photoactive layer being a bulk heterojunction (BHJ).

Figure 5 shows the current-voltage curve with a BHJ cell having the following construction: ITO / C60 (15 nm) / compound **8**:C60 (20/30 nm, 3:2, 70°C) / BPAPF (10 nm) / BPAPF:NDP9 (30 nm, 9.7%wt) / NDP9 (1 nm) / Au (50 nm), the photoactive layer being a bulk heterojunction (BHJ).

Figure 6 shows the current-voltage curve with a BHJ cell having the following construction: ITO / C60 (15 nm) / compound **10**:C60 (20/30 nm, 3:2, 50°C) / BPAPF (10 nm) / BPAPF:NDP9 (30 nm, 10.6%wt) / NDP9 (1 nm) / Au (50 nm), the photoactive layer being a bulk heterojunction (BHJ).

Figure 7 shows an exemplary photoactive device with a substrate 1, made of glass, for example, on which there is a cathode as electrode 2, which may comprise ITO, for example. Arranged thereon are an electron-transporting layer 3 as ETL and also a photoactive layer 4, comprising the inventive compounds as p-conducting donor component and, additionally, an n-conducting component as electron acceptor

component, e.g., C60, either as a planar heterojunction or as a bulk heterojunction. Arranged above these is a hole-conducting layer 5 as HTL, and the anode 6.

Photoactive components with the compounds of the invention may
5 comprise further functional layers and may for example also be designed as multiple cells or tandem cells.

In the text below, the syntheses of the specific exemplary embodiments, and a general synthesis pathway according to the modular system for the inventive compounds, will additionally be elucidated.

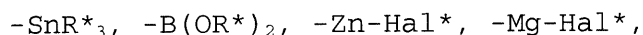
10 Synthesis

The absorber molecules of the invention can advantageously be made available easily and in good yields according to a simple modular system. Depicted below by way of example is the synthesis of the inventive compound of the general formula (I).

15 The general compound **(I)** can be synthesized according to one of the methods described below. This synthesis is intended to act here as an exemplary representation, and may be varied in the sequence of its individual steps, or modified by other known methods. The amalgamation of individual reaction steps, or the alteration to parts
20 of the synthesis route, is also possible.

The substituent "Hal-" stands for halogen component, typically comprising a halogen atom, or else other functional groups which can be used in cross-coupling reactions, such as, for example, carboxylic acids or triflates, or further suitable groups including -H.

25 The substituent "Met-" stands for metal component, referring in the wider sense to metal-containing or semi-metal-containing functional groups or to other functional groups, including those which are metal-free, which can be used in cross-coupling reactions, and including -H. This Met group may more particularly be selected from
30 one of the following functional groups:

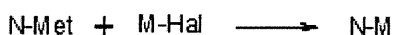


where R* is a C₁-C₁₀ alkyl and where the group "Hal*" is a halogen, selected more particularly from the group containing: Cl, Br, I.

The building block Z of the general compound (I) containing M-N or N-M may therefore be prepared via C-C coupling reactions which are known to the skilled person:



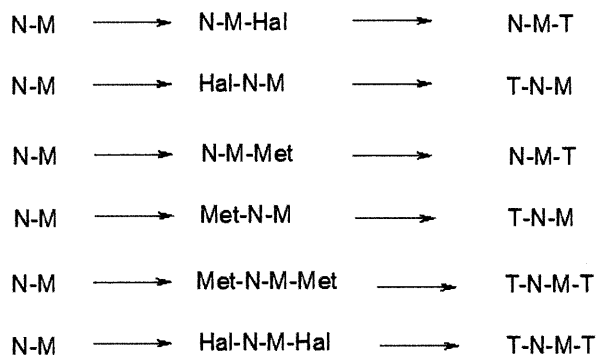
or



5 "Hal" here denotes a halogen substituent, more particularly selected from the group containing: Cl, Br, I. The starting compounds to be used for these reactions are either available commercially or can be obtained by typical metalation or halogenation reactions. The coupling to give the building block N-M or M-N may be carried out,
10 for example, by Suzuki, Negishi or Stille, Kumada or Hiyama and further coupling reactions, which are described in sources including "Metal-Catalyzed Cross-Coupling Reactions, 2nd, Completely Revised and Enlarged Edition" (Wiley VCH, ISBN: 978-3-527-30518-6) (Suzuki: pages 41-123, Negishi: pages 619-670, Stille: pages 125-161, Kumada:
15 pages 671-698, Hiyama: pages 163-216, further coupling reactions: pages 815-889). Generally, but not exclusively, the C-C cross-coupling reactions take place with use of a catalyst.

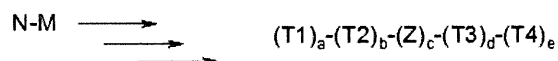
The introduction of further groups selected from N, M or T1 to T4 may be accomplished in turn by metalating one of the two components and
20 halogenating or otherwise substituting the second coupling component, in order to effect activation suitably for C-C coupling reactions. In principle here it is possible to vary which coupling component is equipped with which activating group. Typically, in C-C coupling reactions, high reaction yields are achieved when the more electron-
25 rich building block carries the "Met substituent" and the more electron-deficient building block carries the "Hal substituent". However, the inverse reaction regime may also lead to good results. The coupling of the further building blocks may then be carried out, again, by coupling reactions known to the skilled person, such as
30 Suzuki, Negishi or Stille, Kumada or Hiyama coupling reactions, for example. The selection of a suitable coupling reaction is made by the skilled person with a view to the necessary reaction conditions and the compatibility thereof with any functional groups present. In these reactions, depending on the realization of the target compound,

one or more building blocks per reaction step can be coupled to the scaffold.

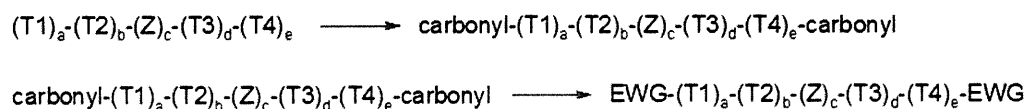


Where one building block T is a component of the formula 11 or
 5 formula 11*, this building block may take place according to a
 customary route known to the skilled person for the introduction of
 double bonds. This route may involve, for example, Heck, Wittig
 and/or aldol reactions, or else eliminations, Cope or McMurry
 reactions, or the aforementioned C-C coupling reactions, which are
 10 described in sources including March's Advanced Organic Chemistry:
 Reactions, Mechanisms, and Structure, 7th Edition (ISBN: 978-0-470-
 46259-1) (chapter 12, pp. 649ff, chapter 13, pp. 732ff, chapter 16,
 pp. 1067ff, chapter 17, pp. 1253ff, chapter 19, pp. 1433ff.).

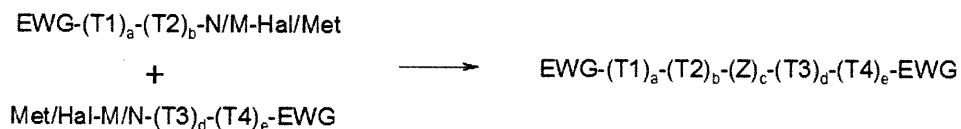
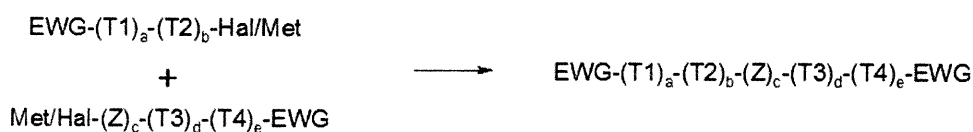
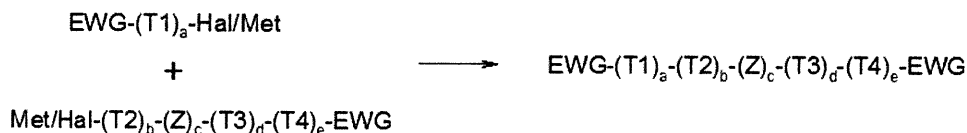
By the methods described it is possible to introduce any desired
 15 further building blocks from the group of N, M or T.



The electron-withdrawing groups EWG1 and EWG2 are generally
 introduced by an aldol condensation of a component of the formulae 7,
 8 or 9, carrying an activated methylene unit, with a carbonyl
 20 component, which is introduced beforehand onto the adjacent moiety T,
 M or N by methods known to the skilled person such as, for example,
 Gattermann, Gattermann-Koch, Houben-Hoesch, Vilsmeier/Vilsmeier-
 Haack, Friedel-Crafts acylation or, following lithiation, by reaction
 with an acid derivative or carbonylation reagent, these being
 25 described in sources including Organikum (ISBN 978-3-527-33968-6 -
 Wiley-VCH, chapters D2-D9).



where the group "carbonyl" is the carbonyl component stated above. The sequence of the synthesis steps described can be varied arbitrarily. Hence it is possible, for example, to build up two molecular moieties of the general formula (I) by one of the methods 5 described above, and to form the bond between the components M-N, N-N, M-M, N-T, M-T or T-T in the last reaction step.



Inventive compounds were synthesized by methods represented below, on the basis either of

- 10 a. dual Stille coupling,
- b. dual inverse Stille coupling, or
- c. simple Stille coupling.

Set out below are the corresponding general operating protocols (GOP1 to GOP3) for versions a, b and c:

15 a) General Operating Protocol (GOP1)

1 mmol of distannyl compound reactant 1 and 2.5 mmol of reactant 2 were dissolved in 4 ml of corresponding solvent (table 4) and the solution was degassed. Then 0.05 mmol of Pd catalyst was added thereto and the reaction mixture was heated overnight. The reaction 20 mixture was brought to room temperature, precipitate which formed in this operation was removed by filtration, and this precipitate was washed with methanol. The crude product was recrystallized from corresponding solvent.

Number	Reactant 1	Reactant 2	Reaction conditions	Yield (%)	Recrystallized from
1	A1	B8	$\text{Pd}(\text{PPh}_3)_4/\text{DMF}/80^\circ\text{C}$	32	Chlorobenzene
2	A1	B6	$\text{Pd}(\text{PPh}_3)_4/\text{DMF}/80^\circ\text{C}$	34	Chlorobenzene
4	A1	B2	$\text{Pd}(\text{PPh}_3)_4/\text{DMF}/80^\circ\text{C}$	27	Chlorobenzene
5	A2	B2	$\text{Pd}(\text{PPh}_3)_4/1,4\text{-dioxane}/80^\circ\text{C}$	34	Chlorobenzene
11	A1	C14	$\text{Pd}_2(\text{dba})_3/\text{P}(\text{tert-Bu})_3/1,4\text{-dioxane}/80^\circ\text{C}$	43	Chlorobenzene

Table 4: Reaction conditions for the synthesis of compounds **1, 2, 4, 5, 11**

b) General Operating Protocol (GOP2)

1 mmol of **dibromo compound** and 2.5 mmol of **B4** were dissolved in 4 ml of dioxane and the solution was degassed. Then 0.05 mmol of Pd catalyst was added thereto and the reaction mixture was stirred at 80°C overnight. The reaction mixture was brought to room temperature, precipitate formed was removed by filtration, and this precipitate was washed with methanol.

Number	Reactant 1	Reactant 2	Reaction conditions	Yield (%)	Recrystallized from
6	A3	B4	$\text{Pd}_2\text{dba}_3 / \text{P}(\text{t-Bu})_3 \cdot \text{HBF}_4 / 80^\circ\text{C}$	40	Chlorobenzene
12	A8	B4	$\text{Pd}_2\text{dba}_3 / \text{P}(\text{t-Bu})_3 / \text{dioxane}/60^\circ\text{C}$	13	Tetrahydrofuran/ hexane

Table 5: Reaction conditions for the synthesis of compound **6 and 12**

c) General Operating Protocol (GOP3)

In a Schlenk vessel rendered inert using argon, 1 mmol of halogen compound reactant 1 and 1.2 mmol of 2-[3-(5-trimethylstannanylfuran-2-yl)allylidene]malononitrile **B4** reactant 2 were dissolved in 3 ml of solvent. The solution was degassed, then 0.05 mmol of Pd catalyst was added and the reaction mixture was heated overnight with stirring. The reaction mixture was cooled to room temperature, the resulting precipitate was removed by filtration, and this precipitate was washed with methanol. The crude product was recrystallized from the respective solvent (table 5).

Number	Reactant 1	Reactant 2	Reaction conditions	Yield/%	Recrystallized from
3	C4	B4	Pd2(dba)3 / P(tBu)3, 1,4-dioxane, 80°C	72	Tetrahydrofuran/ hexane
7	C6	B4	Pd2(dba)3 / P(tBu)3, 1,4-dioxane, 80°C	62	Tetrahydrofuran
8	C10	B4	Pd2(dba)3 / P(tBu)3, 1,4-dioxane, 80°C	26	Tetrahydrofuran/ hexane
9	C2	B4	Pd(PPh ₃) ₄ , tetrahydrofuran, 65°C	9	Tetrahydrofuran/ hexane
10	C8	B4	Pd2(dba)3 / P(tBu)3, 1,4-dioxane, 80°C	48	Tetrahydrofuran/ hexane
13	C25	B4	Pd2(dba)3 / P(tBu)3, 1,4-dioxane, 80°C	20	Purified by column chromatography (dichloromethane)
14	C27	B4	Pd(PtBu ₃) ₂ 1,4-dioxane, 80°C	39	Toluene
15	C37	B4	Pd(PtBu ₃) ₂ 1,4-dioxane, 60°C	59	Toluene
16	C23	B4	Pd(PtBu ₃) ₂ , 1,4-dioxane, 60°C	55	Chlorobenzene
17	C39	B4	Pd(PtBu ₃) ₂ , 1,4-dioxane, 60°C	80	Tetrahydrofuran/ hexane

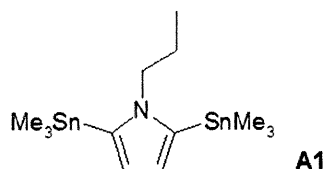
Table 6: Reaction conditions for the synthesis of compounds **3**, **7**, **8**, **9**, **10**, **13** to **17**

Alternatively it is also possible for inventive compounds to take place via other known C-C coupling reactions such as, for example, Suzuki or Negishi reaction.

The reactants 1 (A), reactants 2 (B) and reactants 3 (C) may be synthesized according to the following protocols:

Synthesis of compounds A1-A19

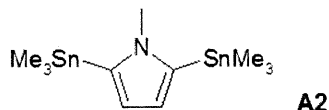
N-Propyl-2,5-bis-trimethylstannyl-pyrrole (A1)



The compound was prepared in accordance with the literature reference of G. H. Jana et al. Bioorg. Med. Chem. Lett., 2015, (15), 3592-3595. Instead of tributyltin chloride, trimethyltin chloride was used.

The crude product was recrystallized from methanol to give product **A1** in 35% yield as a colorless solid. ¹H-NMR (CDCl₃): 6.40 ppm (s, 2H), 3.88 (m, 2H), 1.76 (m, 2H), 0.97 (t, 3H), 0.32 (s, 18H).

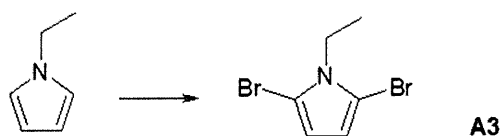
10 N-Methyl-2,5-bis-trimethylstannyl-pyrrole (A2)



The compound was prepared in accordance with the literature reference of G. H. Jana et al. Bioorg. Med. Chem. Lett., 2015, (15), 3592-3595. Instead of tributyltin chloride, trimethyltin chloride was used.

15 The crude produce was recrystallized from isopropanol to give product **A2** in 34% yield as a colorless solid. ¹H-NMR (CDCl₃): 6.39 ppm (s, 2H), 3.75 (s, 3H), 0.32 (s, 18H).

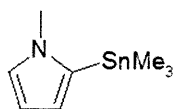
2,5-Dibromo-1-ethyl-pyrrole (A3)



20 951 mg (10.0 mmol) of 1-ethylpyrrole were dissolved in 50 ml of THF at -78°C under an argon atmosphere. 3.60 g (20.0 mmol) of NBS were added over the course of 15 minutes. The reaction mixture was stirred at -78°C for 4 hours and then warmed to RT overnight. The reaction mixture was admixed with 100 ml of saturated Na₂SO₃ solution and
 25 extracted twice with MTBE. The combined organic phases were washed with saturated NaCl solution. They were dried over Na₂SO₄ and filtered

and the solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel to 1.00 g of product **A3** (40%) as a colorless oil. GC-MS (EI, 75 eV) m/z 252.9 (M^+ , 100%).

1-Methyl-2-trimethylstannanyl-1H-pyrrole (A4)

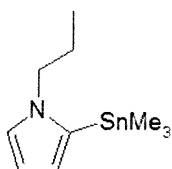


5

A4

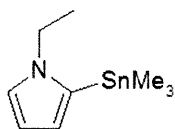
The synthesis took place in analogy to Groenendaal *et al.* Synth. Commun. 1995, 25 (10), 1589-1600

1-Propyl-2-trimethylstannanyl-1H-pyrrole (A5)

**A5**

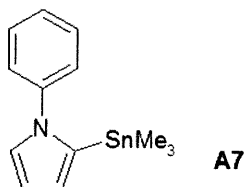
10 The synthesis took place in analogy to Groenendaal *et al.* Synth. Commun. 1995, 25 (10), 1589-1600

1-Ethyl-2-trimethylstannanyl-1H-pyrrole (A6)

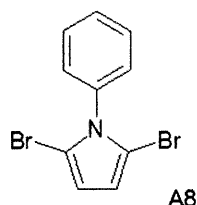
**A6**

The synthesis took place in analogy to Groenendaal *et al.* Synth. Commun. 1995, 25 (10), 1589-1600

1-Phenyl-2-trimethylstannanyl-1H-pyrrole (A7)

**A7**

The synthesis took place in analogy to Groenendaal *et al.* Synth. Commun. 1995, 25 (10), 1589-1600

2,5-Dibromo-1-phenyl-pyrrole (A8)

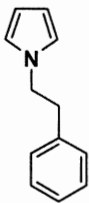
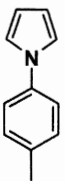
1446 mg (10.0 mmol) of 1-phenylpyrrole were dissolved in 50 ml of THF at -78°C under an argon atmosphere. 3.60 g (20.0 mmol) of NBS were added over the course of 15 minutes. The reaction mixture was stirred at -78°C for 4 hours and then warmed to RT overnight. The reaction mixture was admixed with 100 ml of saturated Na_2SO_3 solution and extracted twice with MTBE. The combined organic phases were washed with saturated NaCl solution. They were dried over Na_2SO_4 and filtered and the solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel to 2.75 g of product **A8** (91%) as a colorless solid. $^1\text{H-NMR}$ (acetone- d_6): 7.57 ppm (m, 3H), 7.31 (dd, 2H), 6.38 (s, 1H).

General protocol for the synthesis of pyrroles from
 15 dimethoxytetrahydrofuran

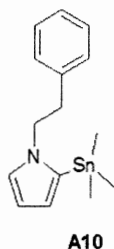
The syntheses take place in analogy to literature protocol from Sunil Kumar *et al.*, J. Phys. Chem. C, 2014, 118 (5), 2570:

50 mmol of sodium acetate were dissolved in 100 ml of demineralized water at room temperature, and 50 mmol of the corresponding amine were added. 25 ml of glacial acetic acid were slowly added dropwise thereto and the mixture was heated to 80°C . 50 mmol of 2,5-dimethoxytetrahydrofuran were added dropwise and the reaction mixture was stirred at 80°C for 16 hours. The reaction solution was then brought to room temperature and extracted with dichloromethane. The organic phase was washed with saturated NaCl solution, dried over sodium sulfate and concentrated on a rotary evaporator. The crude product was purified by chromatography.

Structure	Number	Yield	Characterization
	A13	82	GC-MS m/z: 177 [M]

	A9	96	GC-MS m/z: 171 [M], 104, 80
	A16	80	GC-MS m/z: 132 [M]

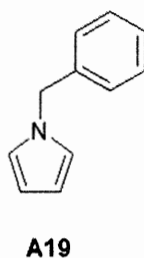
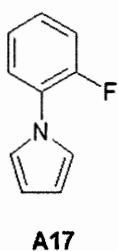
Synthesis of 1-phenethyl-2-trimethylstannyl-1H-pyrrole (A10)



The synthesis of A10 took place in analogy to Groenendaal *et al.*
 5 Synth. Commun. 1995, 25 (10), 1589-1600

1-(2-Fluoro-phenyl)-1H-pyrrole (A17)

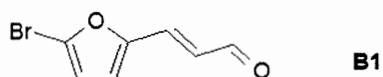
1-Benzyl-1H-pyrrole (A19)



The compounds A17 and A19 are available commercially.

10 Synthesis of the compounds B1-B8

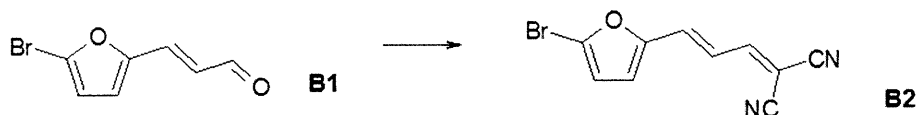
(E)-3-(5-Bromo-furan-2-yl)-propenal (B1)



The synthesis of **B1** takes place according to the literature reference of I. I. Popov, Z. N. Nazarova, A. P. Chumak, Chem. Heterocycl. Compd., 1978, 14, (3), 253-255:

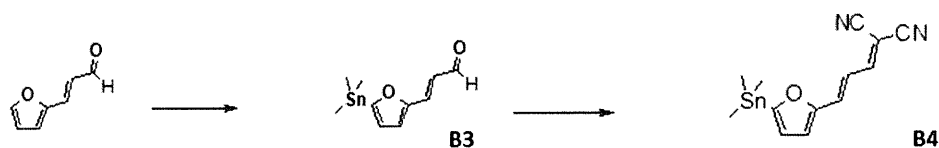
50 mmol of 5-bromo-2-furfural were suspended in 100 ml of 6% NaOH solution. Acetaldehyde in 15 ml of water was added dropwise to the reaction mixture at 0°C. Stirring was continued at 0°C for 1 hour. The precipitate was isolated by filtration, washed with water and dried. The crude product was purified by chromatography on silica gel. Yield 74%. ¹H-NMR (acetone-d₆): 9.64 ppm (d, 1H), 7.44 (d, 1H), 7.04 (d, 1H), 6.73 (d, 1H), 6.47 (dd, 1H).

(E)-3-(5-Bromo-furan-2-yl)-allylidene]-malononitrile (**B2**)



36.7 mmol of (E)-3-(5-bromo-furan-2-yl)-propenal and 44.0 mmol of malonitrile were dissolved in 50 ml of ethanol. 3.7 mmol of β-alanine were added thereto and the reaction mixture was stirred at room temperature for 24 hours. The precipitate formed was briefly heated to boiling and then cooled in an ice bath. The solid which crystallized out was isolated by filtration and washed with a little ethanol. Drying in a desiccator led to the isolation of 3.49 g of [(E)-3-(5-bromo-furan-2-yl)-allylidene]-malononitrile **B2** (38% yield). EI m/z: 250[M], 169, 141, 114.

(E)-3-(5-Trimethylstannyl-furan-2-yl)-propenal (**B3**)



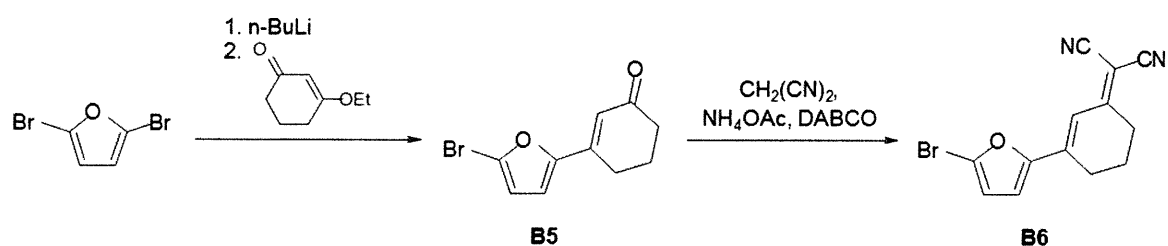
A solution of 3.06 g (29.9 mmol) of 1-methylpiperazine in 82 ml of anhydrous THF was admixed dropwise under an argon atmosphere and at -78°C with 12 ml (30 mmol) of n-butyllithium solution (2.5M in hexane). After 15 minutes of stirring, 3.15 g (25.0 mmol) of trans-3-(2-furyl)acrolein were added dropwise. After a further 15 minutes of stirring, 3.95 g (33.7 mmol) of N,N,N',N'-tetramethylethylenediamine were added dropwise. After 15 minutes of stirring, 13.4 ml (33.5 mmol) of n-butyllithium solution (2.5M in hexane) were added

dropwise. The reaction mixture was stirred at -20°C for 3 hours and then cooled again to -78°C . At this temperature, 29.9 ml (29.9 mmol) of a 1M solution of trimethyltin chloride in THF were added and the mixture was subsequently stirred at R.T. for 16 hours. Then 100 ml of water were added, the organic phase was removed, the aqueous phase was extracted three times with MTBE, and the combined organic phases were washed with 80 ml each of 1M hydrochloric acid, saturated ammonium chloride solution and brine. After drying over sodium sulfate, the solvents were removed by distillation and the residue was purified by chromatography (SiO_2 , petroleum ether/MTBE 5/1). Yield 5.52 g (76%). $^1\text{H-NMR}$ (400 MHz) in acetone- d_6 : 0.38 (s, 9H), 6.48 (dd, 1H), 6.84 (d, 1H), 6.97 (d, 1H), 7.51 (d, 1H), 9.63 (d, 1H).

2-[(E)-3-(5-Trimethylstannanyl-furan-2-yl)-allylidene]-malononitrile (B4)

Under an argon atmosphere, 9.52 g (33.4 mmol) of **B3** and 2.23 g (33.4 mmol) of malodinitrile were dissolved in 19 ml of ethanol. 152 mg (1.67 mmol) of beta-alanine were added and the mixture was stirred at R.T. for 4 hours. It was then heated to reflux temperature and cooled slowly to 0°C with stirring. The precipitate was isolated by filtration, washed with 2 ml of ethanol and dried under reduced pressure: 9.10 g (82%) of orange crystalline solid. $^1\text{H-NMR}$ (400 MHz) in acetone- d_6 : 0.41 (s, 9H), 6.90 (d, 1H), 7.07 (m, 2H), 7.46 (d, 1H), 8.01 (d, 1H).

3-(5-Bromo-furan-2-yl)-cyclohex-2-enone (B5)



25

Under an argon atmosphere, a solution of 2.00 g of 2,5-dibromofuran (8.85 mmol) in 25 ml of diethyl ether was admixed dropwise at -65°C and with stirring with 5.53 ml of n-butyllithium (1.6M in hexane) over the course of 15 minutes. After a further 15 minutes, 1.86 g of 3-ethoxy-2-cyclohexen-1-one (13.3 mmol) were added and the mixture was heated overnight at R.T. The mixture was added to 150 ml of brine and extracted with 3 x 100 ml of dichloromethane. The combined

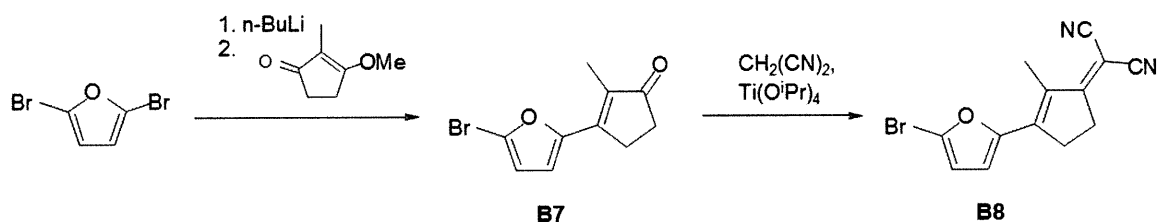
30

organic extracts were washed with 2M hydrochloric acid and dried over sodium sulfate and the solvents were removed under reduced pressure. Purification by column chromatography (SiO_2 , dichloromethane) gave **B5** as a yellow crystalline solid (1.08 g, 4.48 mmol, 51%). $^1\text{H-NMR}$ (CDCl_3): 6.68 ppm (d, 1H), 6.44-6.43 (m, 2H), 2.60 (td, 2H), 2.46 (t, 2H), 2.14-2.07 (m, 2H).

2-[3-(5-Bromo-furan-2-yl)-cyclohex-2-enylidene]-malononitrile (B6)

Under an argon atmosphere, 1.68 g of ammonium acetate (21.8 mmol) were added to a solution of 1.74 g of **B5** (7.14 mmol) and 1.42 g of malononitrile (21.5 mmol) in dichloroethane. The mixture was refluxed for 2 hours, then 20 mg of 1,4-diazabicyclo[2.2.2]octane (0.178 mmol) were added, followed by refluxing for a further 16 hours. The reaction mixture was added to 100 ml of water and extracted with 3 x 50 ml of dichloromethane. The combined organic extracts were washed with 100 ml of water and dried over sodium sulfate and the solvents were removed under reduced pressure. Purification by column chromatography (SiO_2 , hexane) gave **B6** as an orange crystalline solid (1.15 g, 3.98 mmol, 91%). $^1\text{H-NMR}$ (CDCl_3): 7.19 ppm (s, 1H), 6.79 (d, 1H), 6.49 (d, 1H), 2.80 (t, 2H), 2.64-2.61 (m, 2H), 2.00-1.94 (m, 2H).

3-(5-Bromo-furan-2-yl)-2-methyl-cyclopent-2-enone (B7)



Under an argon atmosphere, a solution of 3.46 g of 2,5-dibromofuran (15 mmol) in 45 ml of diethyl ether was admixed dropwise at -65°C and with stirring with 6.00 ml of n -butyllithium (2.5M in hexane, 15 mmol) over the course of 30 minutes. After a further 15 minutes, 2.94 g of 3-ethoxy-2-methyl-2-cyclopenten-1-one (21.0 mmol) in solution in 15 ml of diethyl ether were added and the mixture was stirred at -65°C for 1.5 hours and then warmed to R.T. overnight. Following the addition of 150 ml of dichloromethane, the mixture was added to 300 ml of 1M hydrochloric acid. The organic phase was removed and the aqueous phase was extracted once with 100 ml of

dichloromethane. The combined organic phases were washed with 2M hydrochloric acid (150 ml) and water (100 ml) and dried over sodium sulfate and the solvents were removed under reduced pressure.

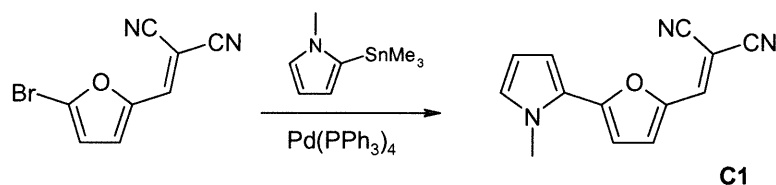
Purification by column chromatography (SiO₂, dichloromethane/hexane) gave **B7** as a yellow crystalline solid (2.10 g, 8.71 mmol, 58%). ¹H-NMR (CDCl₃): 6.75 ppm (d, 1H), 6.50 (d, 1H), 2.86-2.82 (m, 2H), 2.52-2.49 (m, 2H), 2.02 (t, 3H).

2-[3-(5-Bromo-furan-2-yl)-2-methyl-cyclopent-2-enylidene]-malononitrile (B8)

A solution of 1.30 g of 3-(5-bromofuran-2-yl)-2-methylcyclopent-2-enone (5.39 mmol) and 3.60 g of malononitrile (53.9 mmol) in 1,2-dichloroethane was admixed under an argon atmosphere with 3.09 g of tetraisopropyl orthotitanate (10.8 mmol) and stirred under reflux for 3 days. The reaction mixture was poured onto hydrochloric acid (1M, 200 ml), stirred vigorously for 30 minutes and extracted with dichloromethane (3 x 100 ml). The combined organic phases were washed with water (100 ml), dried over sodium sulfate and filtered, and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, dichloromethane) gave **B8** (1.37 mg, 4.75 mmol, 88%) as an orange-colored crystalline solid. ¹H-NMR (CDCl₃): 6.82 ppm (d, 1H), 6.55 (d, 1H), 3.09-3.06 (m, 2H), 3.00-2.96 (m, 2H), 2.40 (t, 3H).

Synthesis of the compounds C1-C39

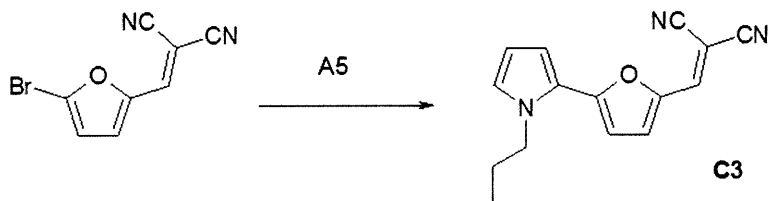
2-[5-(1-Methyl-1H-pyrrol-2-yl)-furan-2-ylmethylene]-malononitrile (C1)



In a baked Schlenk vessel, **C12** (1.01 g, 4.52 mmol) and **A4** (849 mg, 3.48 mmol) were introduced under argon in dry tetrahydrofuran (5 ml), and tetrakis-(triphenylphosphine)-palladium(0) (101 mg, 87 μmol) was added. The reaction mixture was stirred at a bath temperature of 80°C for 16 hours, poured onto water (about 150 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic phases were dried over sodium sulfate and filtered and the solvent was removed under

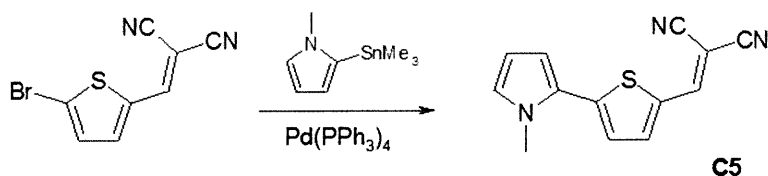
reduced pressure. Purification by column chromatography (silica gel, dichloromethane/petroleum ether) afforded **C1** (420 mg, 1.88 mmol, 54%) as a red crystalline solid. $^1\text{H-NMR}$ (acetone- D_6): 7.84 ppm (s, 1H), 7.52 (d, 1H), 7.03-7.02 (m, 1H), 6.97 (d, 1H), 6.90 (dd, 1H), 6.21 (dd, 1H), 4.00 (s, 3H).

2-[5-(1-Propyl-1H-pyrrol-2-yl)-furan-2-ylmethylene]-malononitrile
(C3)



In a baked Schlenk vessel, **C12** (669 mg, 3.00 mmol) and **A5** (1.10 g, 3.00 mmol) were introduced under argon in dry tetrahydrofuran (5 ml), and tetrakis-(triphenylphosphine)-palladium(0) (87 mg, 75 μmol) was added. The reaction mixture was stirred at a bath temperature of 70°C for 16 hours, poured onto about 150 ml of water and extracted with dichloromethane (3 x 100 ml). The combined organic phases were dried over sodium sulfate and filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, dichloromethane/petroleum ether) afforded **C3** (500 mg, 1.99 mmol, 66%) as an orange-colored viscous oil. $^1\text{H-NMR}$ (acetone- d_6): 7.85 ppm (s, 1H), 7.53 (d, 1H), 7.10 (dd, 1H), 6.95-6.93 (m, 2H), 6.23 (dd, 1H), 4.36 (t, 2H), 1.75 (sext, 2H), 0.88 (t, 3H).

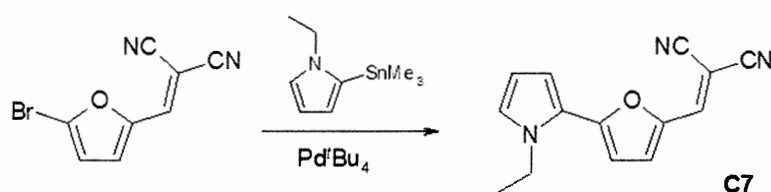
2-[5-(1-Methyl-1H-pyrrol-2-yl)-thiophen-2-ylmethylene]-malononitrile
(C5)



In a baked Schlenk vessel, **C11** (1.09 g, 4.55 mmol) and **A4** were introduced under argon in dry tetrahydrofuran (7 ml), and tetrakis-(triphenylphosphine)-palladium(0) (105 mg, 91 μmol) was added. The reaction mixture was stirred at a bath temperature of 80°C for 16 hours, poured onto water (about 150 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic phases were dried

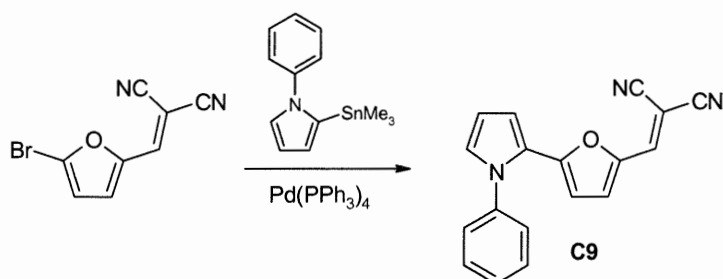
over sodium sulfate and filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, dichloromethane/petroleum ether) afforded **C5** (670 mg, 2.80 mmol, 80%) as a red crystalline solid. $^1\text{H-NMR}$ (CDCl_3): 7.74 ppm (s, 1H), 7.66 (d, 1H), 7.19 (d, 1H), 6.84-6.82 (m, 1H), 6.68 (dd, 1H), 6.23 (dd, 1H), 3.87 (s, 3H).

2-[5-(1-Ethyl-1H-pyrrol-2-yl)-thiophen-2-ylmethylene]-malononitrile (C7)



In a baked Schlenk vessel, **C12** (989 mg, 4.43 mmol) and **A6** (1.10 g, 3.41 mmol) were introduced under argon in dry dioxane (5 ml) and degassed for 10 minutes, and tris-(dibenzylideneacetone)-dipalladium(0) (81 mg, 85 μmol) and tri-*tert*-butylphosphine tetrafluoroborate (100 mg, 341 μmol) were added. The reaction mixture was stirred at a bath temperature of 80°C for 16 hours, poured onto water (about 150 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic phases were dried over sodium sulfate and filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, dichloromethane) afforded **C7** (820 mg, 3.46 mmol, 78%) as a red solid. $^1\text{H-NMR}$ (acetone- D_6): 7.85 ppm (s, 1H), 7.54 (d, 1H), 7.12-7.11 (m, 1H), 6.98 (d, 1H), 6.94-6.93 (m, 1H), 6.25-6.23 (m, 1H), 4.43 (q, 2H), 1.39 (t, 3H).

2-[5-(1-Phenyl-1H-pyrrol-2-yl)-furan-2-ylmethylene]-malononitrile (C9)



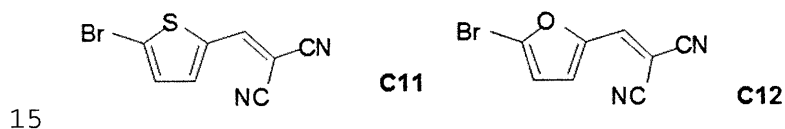
In a baked Schlenk vessel, **C12** (1.45 g, 6.50 mmol) and **A7** (1.91 mg, 5.00 mmol) were introduced in dry 1,4-dioxane (7.5 ml) under argon.

Tri-*tert*-butylphosphine tetrafluoroborate (147 mg, 0.50 mmol) and tris-(dibenzylideneacetone)-dipalladium(0) (118 mg, 125 μ mol) are added. The reaction mixture was stirred at a bath temperature of 80°C for 16 hours, poured onto water (about 150 ml) and extracted with
 5 dichloromethane (3 x 100 ml). The combined organic phases were dried over sodium sulfate and filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, dichloromethane/petroleum ether) gave 2-[5-(1-phenyl-1H-pyrrol-2-yl)-furan-2-ylmethylene]malononitrile (1.35 g, 4.73 mmol, 94%) as a red
 10 crystalline solid.

¹H-NMR (acetone- D_6): 7.82 ppm (s, 1H), 7.59 (m, 3H), 7.47 (m, 2H), 7.28 (d, 1H), 7.17 (m, 1H), 7.07 (m, 1H), 6.47 (m, 1H), 5.57 (d, 1H).

2-(5-Bromo-thiophen-2-ylmethylene)-malononitrile (C11)

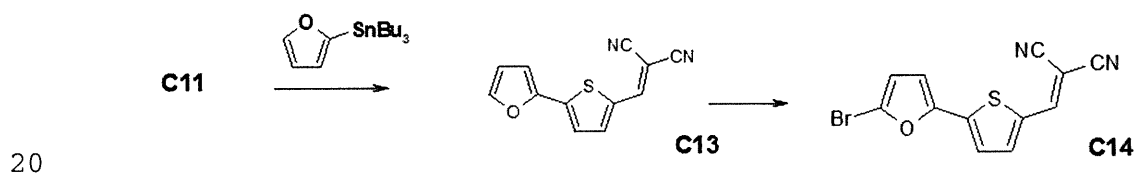
2-(5-Bromo-furan-2-ylmethylene)-malononitrile (C12)



Compounds C11 and C12 are prepared in accordance with the literature-described synthesis (Qi et al., J. Mat. Chem. 2008, 18, 1131).

2-(5-Furan-2-yl-thiophen-2-ylmethylene)-malononitrile (C13)

2-[5-(5-Bromo-furan-2-yl)-thiophen-2-ylmethylene]-malononitrile (C14)



2-(5-Furan-2-yl-thiophen-2-ylmethylene)-malononitrile (C13)

In a baked Schlenk vessel, C11 (2.39 g, 10.0 mmol) and 2-tributylstannylfuran (4.79 g, 13.0 mmol) in dry 1,4-dioxane (14.9 ml)
 25 were introduced under argon. Tri-*tert*-butylphosphine tetrafluoroborate (293 mg, 1.00 mmol) and tris-(dibenzylideneacetone)-dipalladium(0) (236 mg, 250 μ mol) are added. The reaction mixture was stirred at a bath temperature of 80°C for 16 hours. The orange suspension was filtered and the residue was

recrystallized from ethanol. This gave product **C13** (1.67 g, 4.73 mmol, 74%) as an orange crystalline solid.

$^1\text{H-NMR}$ (CDCl_3): 7.78 ppm (s, 1H), 7.67 (d, 1H), 7.55 (d, 1H), 7.36 (d, 1H), 6.85 (d, 1H), 6.56 (dd, 1H).

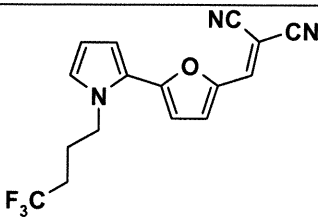
5 2-[5-(5-Bromo-furan-2-yl)-thiophen-2-ylmethylene]-malononitrile (C14)

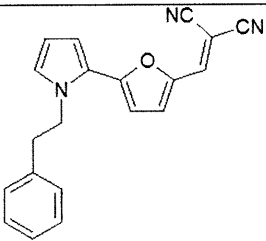
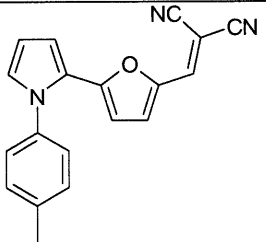
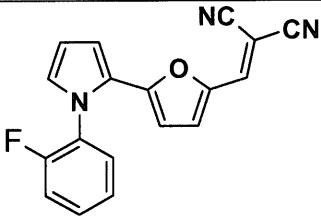
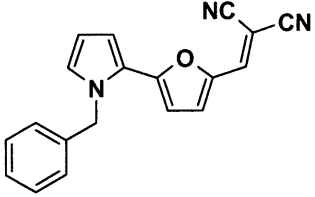
2-(5-Furan-2-yl-thiophen-2-ylmethylene)-malononitrile (**C13**) (1.11 g, 4.86 mmol) was introduced under argon in dry tetrahydrofuran (44 ml) at -70°C , and N-bromosuccinimide (874 mg, 4.86 mmol) was added. The reaction mixture was stirred at -70°C in the absence of light for 10 30 minutes and was gradually warmed to room temperature overnight in a cold bath. Following the addition of 50 ml of water, the product was isolated by filtration and dried. The residue was recrystallized from ethanol to give the product **C14** (1200 mg, 3.93 mmol, 81%) as an orange crystalline solid.

15 $^1\text{H-NMR}$ (CDCl_3): 7.78 ppm (s, 1H), 7.66 (d, 1H), 7.35 (d, 1H), 6.79 (d, 1H), 6.49 (d, 1H).

General protocol for bromination and Stille coupling

1 mmol of the corresponding pyrrole was dissolved in 25 ml of dry THF and cooled to -78°C under argon. 0.8 mmol of NBS, in solution in 20 10 ml of dry THF, was slowly added dropwise at -78°C and the reaction mixture was stirred at -78°C for 2 hours. The mixture was subsequently brought to room temperature and 35 ml of dioxane, 1.2 mmol of 2-(5-trimethylstannanyl-furan-2-ylmethylene)-malononitrile (C18) and 1 mol% of $\text{Pd}[\text{P}(\text{t-Bu}_3)]_2$ were added. The 25 reaction mixture was stirred at 80°C for 16 hours. Purification by column chromatography (silica gel, dichloromethane) afforded the corresponding product.

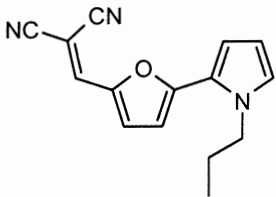
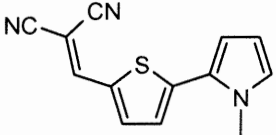
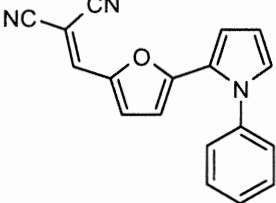
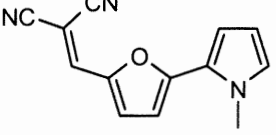
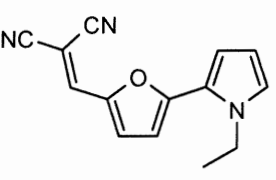
Structure	Number	Reactant	Yield	Characterization
	C26	A13	58%	GC-MS m/z: 319 [M], 222, 180, 104, 77

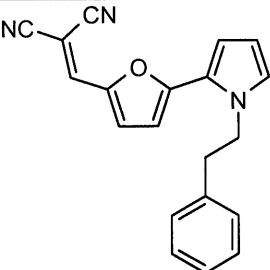
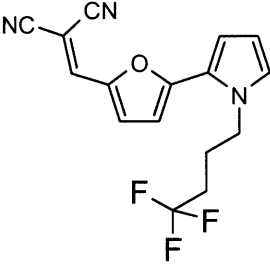
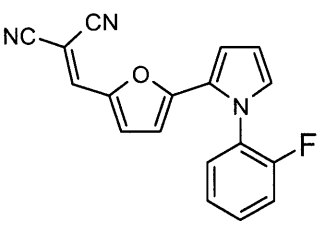
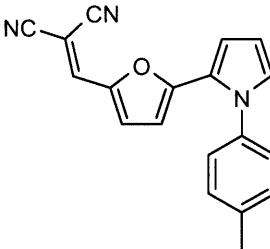
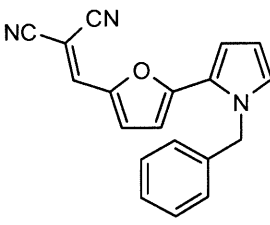
Structure	Number	Reactant	Yield	Characterization
	C24	A10	55%	¹ H-NMR (CDCl ₃) ppm: 7.28 (s, 1H), 7.20 (m, 5H), 6.96 (d, 2H), 6.82 (d, 1H), 6.62 (d, 2H), 6.18 (d, 1H), 4.60 (t, 2H), 3.03 (t, 2H).
	C22	A16	32%	¹ H-NMR (acetone-d ₆): 7.82 ppm (s, 1H), 7.41 (m, 2H), 7.34 (m, 2H), 7.25 (d, 1H), 7.13 (m, 1H), 7.05 (m, 1H), 6.45 (m, 1H), 5.57 (d, 1H), 2.46 (s, 3H).
	C36	A17	40%	¹ H-NMR (DMSO-d ₆): 8.08 ppm (s, 1H), 7.59-7.66 (m, 2H), 7.52 (t, 1H), 7.42 (t, 1H), 7.31 (m, 2H), 6.96 (m, 1H), 6.52 (m, 1H), 5.58 (d, 1H).
	C38	A19	25%	¹ H-NMR (acetone-d ₆): 7.82 ppm (s, 1H), 7.41 (m, 1H), 7.30 (m, 2H), 7.23 (m, 2H), 7.06 (m, 2H), 6.99 (d, 1H), 6.76 (d, 1H), 6.34 (d, 1H), 5.65 (s, 2H).

General protocol for bromination

1 mmol of reactant 1 was introduced under argon in dry tetrahydrofuran (10 ml) at -70°C, and N-bromosuccinimide (178 mg,

1 mmol) was added. The reaction mixture was stirred in the absence of light and gradually warmed to room temperature overnight in a cold bath. Following the addition of triethylamine (1 ml), the solvent was removed under reduced pressure. Purification by column chromatography (silica gel, dichloromethane) afforded the corresponding brominated product.

Product	Reactant 1		Yield/%	Analysis
C4		C3	82	$^1\text{H-NMR}$ (CDCl_3): 7.31-7.28 ppm (m, 2H), 6.83 (d, 1H), 6.64 (d, 1H), 6.31 (d, 1H), 4.34 (t, 2H), 1.73 (sext, 2H), 0.92 (t, 3H).
C6		C5	78	$^1\text{H-NMR}$ (CDCl_3): 7.75 ppm (s, 1H), 7.68 (d, 1H), 7.16 (d, 1H), 6.61 (d, 1H), 6.31 (d, 1H), 3.81 (s, 3H).
C10		C9	37	$^1\text{H-NMR}$ (acetone- D_6): 7.84 ppm (s, 1H), 7.68-7.70 (m, 3H), 6.46 (m, 2H), 7.23 (d, 1H), 7.04 (d, 1H), 6.60 (d, 1H), 5.27 (d, 1H).
C2		C1	93	$^1\text{H-NMR}$ (CDCl_3): 7.30 ppm (s, 1H), 7.26-7.25 (m, 1H), 6.79 (d, 1H), 6.68 (d, 1H), 6.32 (d, 1H), 3.94 (s, 3H).
C8		C7	50	$^1\text{H-NMR}$ (acetone- D_6): 7.91 ppm (s, 1H), 7.56 (d, 1H), 7.05 (d, 1H), 6.98 (d, 1H), 6.41 (d, 1H), 4.49 (q, 2H), 1.33 (t, 3H).

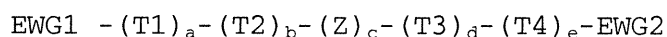
Pro- duct	Reactant 1		Yield/%	Analysis
C25		C2 4	94	$^1\text{H-NMR}$ (CDCl_3) ppm: 7.93 (s, 1H), 7.57 (d, 1H), 7.08 (d, 1H), 6.99 (d, 1H), 6.44 (d, 1H), 4.59 (t, 2H), 2.35 (m, 2H), 1.99 (m, 2H).
C27		C2 6	95	$^1\text{H-NMR}$ (acetone- D_6) ppm: 7.28 (s, 1H), 7.17 (m, 4H), 6.96 (d, 2H), 6.74 (d, 1H), 6.49 (d, 1H), 6.32 (d, 1H), 4.64 (t, 2H), 2.97 (m, 2H).
C37		C3 6	80	$^1\text{H-NMR}$ (acetone- D_6): 7.86 ppm (s, 1H), 7.75-7.81 (m, 1H), 7.63 (m, 1H), 7.53 (m, 2H), 7.28 (d, 1H), 7.08 (d, 1H), 6.67 (d, 1H), 5.47 (d, 1H).
C23		C2 2	79	$^1\text{H-NMR}$ ($\text{DMSO}-\text{D}_6$): 8.09 ppm (s, 1H), 7.45 (d, 2H), 7.34 (d, 2H), 7.25 (d, 1H), 6.89 (d, 1H), 6.66 (d, 1H), 5.20 (d, 1H), 2.45 (s, 3H).
C39		C3 8	74	$^1\text{H-NMR}$ ($\text{DMSO}-\text{D}_6$): 7.99 ppm (s, 1H), 7.44 (d, 1H), 7.31 (m, 2H), 7.24 (m, 1H), 6.98 (m, 3H), 6.84 (d, 1H), 6.55 (d, 1H), 5.62 (s, 2H).

The invention is not confined by the description with reference to the working examples. The invention instead embraces every new feature and also every combination of features, including in

particular every combination of features in the claims, even if that feature or that combination itself is not given explicitly in the claims or working examples.

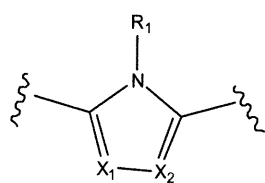
Claims

1. Compounds of the general formula I:

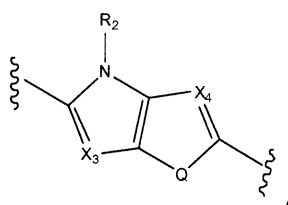


- with the parameters a, b, d and e being each independently of one another 0 or 1,
- with the parameter c being 1, 2, 3, 4 or 5,
- where the general group Z is a block of two groups M and N, linked as *-M-N-* or *-N-M-*, where * designates the attachment to the groups T1 to T4 or EWG1 and EWG2,
- where the groups M each independently of one another are selected from:

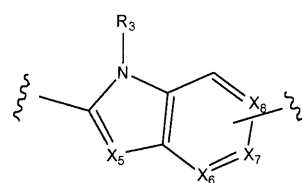
Formula 1



Formula 2

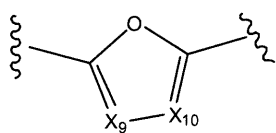


Formula 3

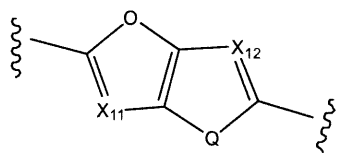


- where the groups N each independently of one another are selected from:

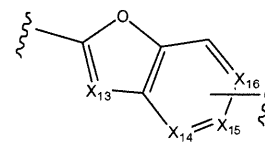
Formula 4



Formula 5



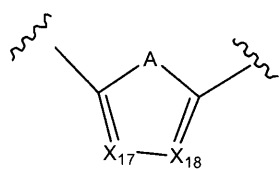
Formula 6



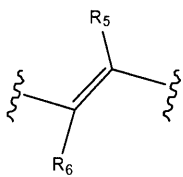
- where M and N are each linked such that at least one N atom of the group M and one O atom of the group N are each joined to one another via 2 C atoms, and $\{$ designates the attachment to the other groups in the compound of the general formula I,
- with X₁-X₁₆ independently of one another being selected from N or C-R, with the proviso that in the groups of the formulae 3 and 6, in each case one group from the groups X₈/X₇ and X₁₆/X₁₅ designates the attachment $\{$ to the other groups in the compound of the general formula I,

- with each R independently of any other being selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted and C atoms of the C₁-C₂₀ alkyl may be replaced by heteroatoms; C₂-C₂₀ alkenyl, O-alkyl, S-alkyl, O-alkenyl, S-alkenyl, alkynyl, aryl, heteroaryl, it being possible for hydrogen atoms to be substituted in all of these groups; CN, NR'R'', with R' and R'' each independently of one another being selected from: H, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted and C atoms of the C₁-C₂₀ alkyl may be replaced by heteroatoms,
- where R₁ to R₃ each independently of one another are selected from a group composed of H, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted and C atoms of the C₁-C₂₀ alkyl may be replaced by heteroatoms; substituted or unsubstituted C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, CN,
- with each Q independently of any other being selected from S, O, Se, NR''', where R''' is defined as for R₁ to R₃,
- where the electron-withdrawing groups EWG1 and EWG2 independently of one another are electron-withdrawing groups having at least one C=C double bond,
- where the groups T1, T2, T3 and T4 each independently of one another are selected from:

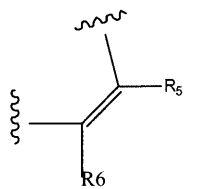
Formula 10



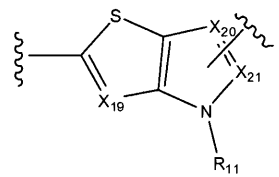
Formula 11



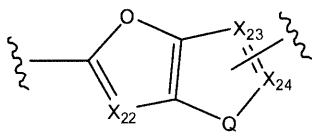
Formula 11*



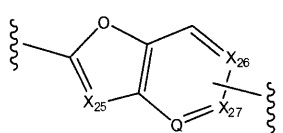
Formula 12



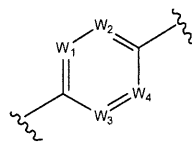
Formula 13



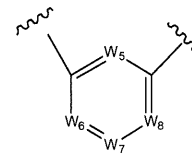
Formula 14



Formula 15



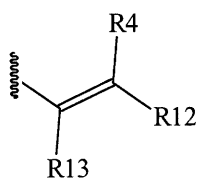
Formula 16



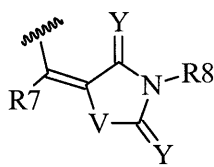
- and ξ designates the attachment to the other groups in the compound of the general formula I,
- with R₅ and R₆ each independently of one another being selected from a group: H, CN, F, aryl, heteroaryl, C₂-C₂₀ alkenyl, alkynyl, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, where, if the substituent R₁₃ is present in the compound of the formula I, a ring closure between R₅ with R₁₃ or R₆ with R₁₃ is possible, with the proviso that between R₅ and R₁₃ or between R₆ and R₁₃ in each case the double bond from formula 11 is located, is possible,
- with W₁ to W₈ each independently of one another being selected from N, CR, where R is defined as described above,
- with X₁₇ to X₂₇ independently of one another being selected from C-R, where R is defined as described above, and with the proviso that in the groups of the formulae 12, 13 and 14, in each case one group from the groups X₂₀/X₂₁, X₂₃/X₂₄ and X₂₆/X₂₇ designates the attachment ξ to the other groups in the compound of the general formula I,
- with A being S, O, NR''''', Se
- with Q being S, O, NR''''', Se
- where for the groups A and Q, the substituent R''''' in each case independently of any other is selected from H, CN, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where the H atoms of the C₁-C₂₀ alkyl may be substituted; C₂-C₂₀ alkenyl, O-alkyl, S-alkyl, O-alkenyl, S-alkenyl, alkynyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl.

2. The compounds of the formula I as claimed in claim 1, where the electron-withdrawing groups EWG1 and EWG2 independently of one another are selected from:

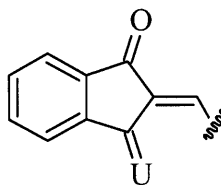
Formula 7



Formula 8



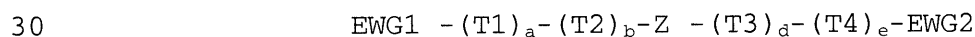
Formula 9



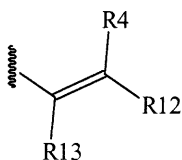
and designates the attachment to the groups T1 to T4 or Z in the compound of the general formula I,

- 5 - with R_4 and R_{12} each independently of one another being selected from H, CN, COOR, with the proviso that R_4 and R_{12} cannot both be H,
- where R is selected from the same group of compounds as defined in the case of R_1 to R_3 ,
- 10 - with each R_{13} independently of any other being selected from a group: H, CN, F, aryl, heteroaryl, C_2 - C_{20} alkenyl, alkynyl, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, where hydrogen atoms of the C_1 - C_{20} alkyl may be substituted, where, if the substituent R_5 or R_6 is present in the compound of the
- 15 formula I, a ring closure between R_5 with R_{13} or R_6 with R_{13} is possible, with the proviso that the double bond from formula 11 is located in each case between R_5 and R_{13} or between R_6 and R_{13} ,
- with V being O, S; with Y being O, S, $C(CN)_2$; with U being O, S, $C(CN)_2$,
- 20 - with R_7 and R_8 each independently of one another being selected from a group H, CN, F, aryl, heteroaryl, C_2 - C_{20} alkenyl, alkynyl, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, where hydrogen atoms of the C_1 - C_{20} alkyl may be
- 25 substituted, where for each of the groups EWG1 and EWG2, each independently of one another in each case for each C=C double bond, both the E-isomer and the Z-isomer may be present.

3. The compounds of the formula I as claimed in claim 1 or 2 with c being 1, having the general formula

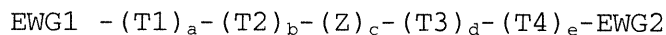


4. The compounds of the formula I as claimed in any of the preceding claims, wherein the electron-withdrawing groups EWG1 or EWG2 are the following group:



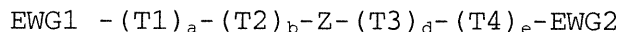
5. The compounds as claimed in the preceding claim, where R_4 and R_{12} are CN.

6. The compounds as claimed in any of the preceding claims, having the general formula

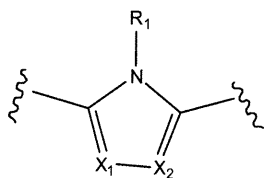


- with one of the indices a , b , d and e being 0.

7. The compounds of the formula I as claimed in any of the preceding claims, with $c = 1$, of the general formula

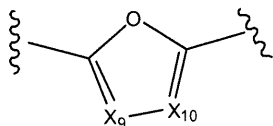


with $\text{Z} = \text{*}-\text{M}-\text{*}$ or $\text{*}-\text{N}-\text{M}-\text{*}$ and M being a group of the formula 1:



8. The compounds of the formula I as claimed in the preceding claim, where X_1 and X_2 independently of one another are selected from C-R with each R independently of any other selected from a group composed of H, halogen, branched or linear, cyclic or open-chain $\text{C}_1\text{-C}_{20}$ alkyl.

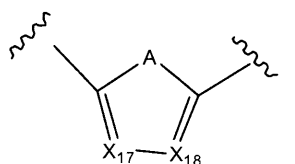
9. The compounds of the formula I as claimed in either of the preceding claims 7 to 8, where the group N is the following general group of the formula 4:



10. The compounds as claimed in the preceding claim, where X_9 and X_{10} independently of one another are selected from C-R with each R

independently of any other being selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl.

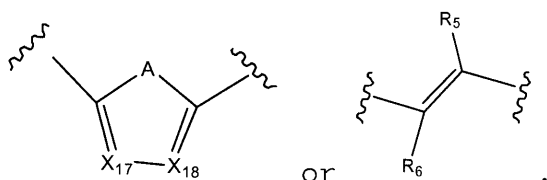
11. The compounds of the formula I as claimed in any of preceding
5 claims 6 to 10, where b is 1 and T2 is the general group of the formula 10



12. The compound of the general formula I as claimed in the preceding claim, wherein A in the formula 10 is S or O.

- 10 13. The compound as claimed in the preceding claim, with X_{17} and X_{18} being C-R, where R independently at each occurrence is selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl.

14. The compounds of the formula I as claimed in any of preceding
15 claims 6 to 13, where d = 1 and the group T3 is selected from the groups of the formulae 10 or 11:



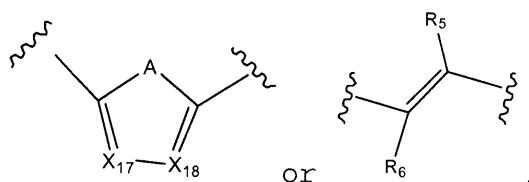
15. The compound of the general formula I as claimed in the preceding claim, where for the formula 10 of claim 13 it is the
20 case that: A = S or O.

16. The compound as claimed in the preceding claim, where X_{17} and X_{18} are C-R, where R independently at each occurrence is selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, R_5 and R_6 each independently of one
25 another are selected from H, CN, F, aryl, heteroaryl, C_2 - C_{20} alkenyl, alkynyl, branched or linear, cyclic or open-chain C_1 - C_{20} alkyl, where hydrogen atoms of the C_1 - C_{20} alkyl may be substituted, where, if the substituent R_5 and R_6 is present in the

compound, a ring closure is possible between R_5 with R_{13} or R_6 with R_{13} , with the proviso that the double bond from formula 11 or formula 11* is located between R_5 and R_{13} or between R_6 and R_{13} .

17. The compound of the general formula I as claimed in the preceding claim, where the ring closure between the substituents R_5 with R_{13} or R_6 with R_{13} is present in the form of an optionally substituted cyclopentenyl ring or of an optionally substituted cyclohexenyl ring.

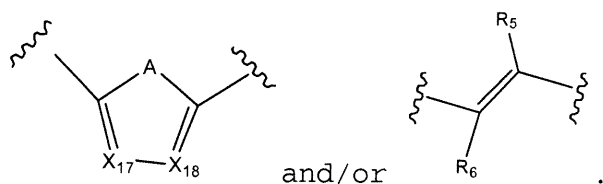
18. The compounds of the formula I as claimed in any of preceding claims 6 to 17, where $d = 1$ and the group T4 is a group of the formula 10 or 11:



19. The compound of the general formula I as claimed in the preceding claim, where $A = O$ or S in the formula 10 of claim 15.

20. The compound as claimed in the preceding claim, where X_{17} and X_{18} are $C-R$, where R is selected independently of any other from a group composed of H , halogen, branched or linear, cyclic or open-chain C_1-C_{20} alkyl.

21. The compounds as claimed in any of preceding claims 6 to 15, where $a = 1$ and the group T1 is selected from the groups of the formulae 10 and/or 11:

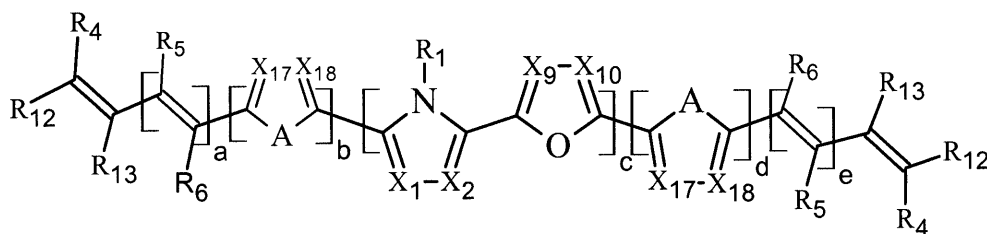


22. The compounds as claimed in the preceding claim, where $A = S$ or O for the formula 10 in claim 16.

23. The compounds as claimed in the preceding claim, where X_{17} and X_{18} are $C-R$, where R independently at each occurrence is selected from a group composed of H , halogen, branched or linear, cyclic

or open-chain C₁-C₂₀ alkyl, R₅ and R₆ are each selected independently of one another from H, CN, F, aryl, heteroaryl, C₂-C₂₀ alkenyl, alkynyl, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, where, if the substituent R₅ and R₆ is present in the compound, a ring closure between R₅ with R₁₃ and also between R₆ with R₁₃ is possible, with the proviso that the double bond from formula 11 or formula 11* is located between R₅ and R₁₃ or between R₆ and R₁₃.

24. The compounds as claimed in claim 1 or 2, having the following general structural formula II:



25. The compounds as claimed in claim 24, where A is O or S independently of one another for A.

26. The compounds as claimed in either of claims 24 and 25, where independently of one another X₁₇, X₁₈, X₁, X₂, X₉ and X₁₀ are C-R, where R independently at each occurrence is selected from a group composed of H, halogen, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, R₅ and R₆ each independently of one another are selected from H, CN, F, aryl, heteroaryl, C₂-C₂₀ alkenyl, alkynyl, branched or linear, cyclic or open-chain C₁-C₂₀ alkyl, where hydrogen atoms of the C₁-C₂₀ alkyl may be substituted, and where, if the substituents R₅ and R₆ are present, a ring closure may be formed between R₅ with R₁₃ or R₆ with R₁₃.
27. The compounds as claimed in any of preceding claims 24 to 26, where c is 1.
28. The compounds as claimed in any of preceding claims 24 to 27, where b is 1.

29. The compounds as claimed in any of preceding claims 24 to 28, where e is 1.
30. The compounds as claimed in any of preceding claims 24 to 29, where R_4 and R_{12} each independently of one another are selected from H, CN, with the proviso that R_4 and R_{12} cannot both be H.
31. The use of one or more compounds as claimed in claims 1 to 30 in an organic electronic component.
32. The use as claimed in claim 31 in an organic photoactive element, preferably in a solar cell.
33. An organic electronic device comprising one or more compounds as claimed in any of claims 1 to 30.
34. The organic electronic device as claimed in the preceding claim, comprising an electrode and a counterelectrode and at least one organic photoactive layer between the electrode and the counterelectrode, where the organic photoactive layer comprises at least one of the compounds as claimed in any of claims 1 to 30.