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(54) Title: DONOR-ACCEPTOR POLYMERS

(57) Abstract: The present invention relates to compounds that are electron-deficient acceptors, donor- acceptor polymers that are synthesized from such electron-deficient acceptors, semiconductor devices synthesized from such donor-acceptor polymers and methods of synthesis of such electron-deficient acceptors, donor-acceptor polymers and semiconductor devices.



Description

Title of Invention: Donor-Acceptor Polymers

Technical Field

5 The present invention generally relates to compounds that may be used as building blocks to construct donor-acceptor polymers. More particularly, the present invention relates to electron-deficient imide-fused pyridazines and imide-fused phthalazines. The present invention also relates to the donor-acceptor polymers constructed using said building blocks and methods for preparing such building blocks and donor-acceptor polymers.

Background Art

10 Organic electronics materials have attracted attention due to their potential in applications such as organic field effect transistors, organic light emitting diodes, organic photovoltaic cells, organic electrochromic materials and sensor materials. However, the commercialization of such devices have been slow due to the lack of suitable materials having high stability, long shelf-life, high performance and a low cost of production.

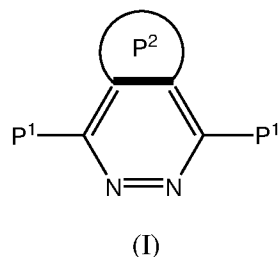
15 Donor-acceptor type conjugated oligomers and polymers have been investigated as organic electronics materials. The physical and optical properties of donor-acceptor type conjugated oligomers and polymers can be conveniently tuned by adjustment of their donor and acceptor moieties.

20 In many applications of organic electronics materials, the electron affinity of the acceptor building blocks is of great importance in tuning the physical and optical properties of the materials and in most cases is crucial to assure the required performance characteristics of the material. The electron affinity plays a vital role in controlling the band-gap of the resultant conjugated polymers. In order to make low band-gap conjugated polymers with desired absorption characteristics for opto-electronic applications, more electron-deficient acceptors especially with high electron deficiency are needed to manufacture organic electronics materials.

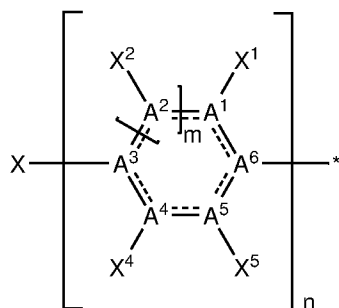
25 There is therefore a need to provide building blocks that overcome, or at least ameliorate, one or more of the disadvantages described above. There is also a need to provide donor-acceptor polymers produced by these building blocks, which may be used as organic electronics materials that overcome, or at least ameliorate, one or more of the disadvantages described above. There is also a need to provide a method of synthesizing building blocks and donor-acceptor polymers that overcome, or at least ameliorate, one or more of the disadvantages described above.

Summary

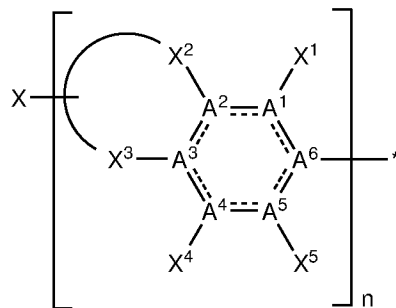
In a first aspect, there is provided a compound having the following Formula (I);



5 wherein P¹ has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

wherein

----- is a single or double bond, as valency allows;

10 m is 0 or 1;

n is an integer selected from 1 to 4;

X, X¹, X², X³, X⁴ and X⁵ are independently absent or selected from the group consisting of a bond, H, halogen, CN, R¹, OR¹ or SR¹;

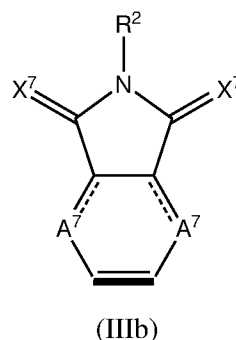
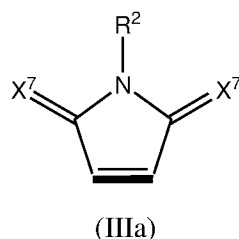
15 wherein R¹ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A¹ is selected from the group consisting of O, S, Se, Te, C and N

A², A³, A⁴, A⁵ and A⁶ are independently C or N; and

20 wherein any two substituents selected from the group consisting of X¹, X², X³, X⁴ and X⁵ may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

25 and wherein P² has the following formula (IIIa) or (IIIb);



wherein

R² is an optionally substituted alkyl or optionally substituted aryl;

5 X⁷ is O or S;

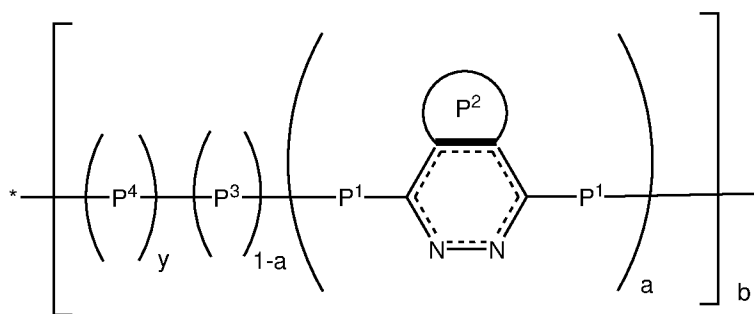
A⁷ is CH, CH₂ or N;

and is where the compound of Formula (IIIa) or (IIIb) is fused to the compound of Formula (I).

Advantageously, the compound of Formula (I) as defined above may combine an electron withdrawing imide group to an electron deficient pyridazine or phthalazine group, resulting in the compound having ultra-high electron affinity. The compound of Formula (I) as defined above may be used as electron-deficient acceptors with unprecedentedly high electron affinity. The compound of Formula (I) as defined above may be even more electron deficient compared to conventional compounds. Further advantageously, the compound of Formula (I) may be easy to functionalize, allowing for fine-tuning of not only its electronic properties but also to enhance its processability. For example, the compound of Formula (I) as defined above may be easily functionalized to improve its solubility. More advantageously, the easily functionalizable nature of the compound of Formula (I) may facilitate its integration with donor compounds. This may be useful, for example, in the manufacture of more processable polymers which may further be used as organic electronic materials.

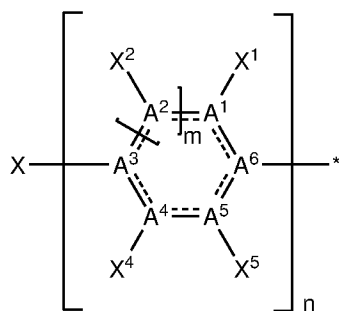
In many applications of organic electronics materials, the electron affinity of the building blocks may be of great importance in tuning the physical and optical properties of the materials and in most cases may be crucial to ensure that the resulting material has the correct characteristics. The electron affinity may play a vital role in controlling the band-gap of the resultant conjugated polymers formed from the electron deficient pyridazine or phthalazine group. Advantageously, by attaching an electron withdrawing imide group to an electron deficient pyridazine or phthalazine group, a compound of Formula (I), which may possess ultra-high electron affinity, may be formed. This building block defined by Formula (I) may be designed to be easily functionalizable and therefore may be of high importance for the development of organic electronics materials. More advantageously, the compound of Formula (I) may be synthesized with a good overall synthetic yield. Further, the compound of Formula (I) may be easily incorporated into donor-acceptor conjugated polymers.

In a second aspect, there is provided a compound having repeating units of the following Formula (IV);

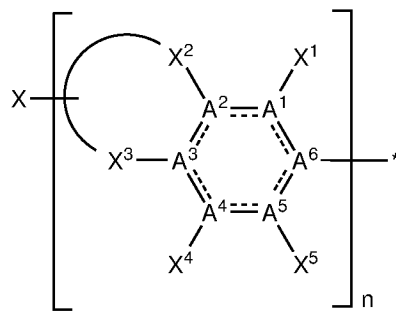


(IV)

wherein P¹ has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

wherein

----- is a single or double bond, as valency allows;

m is 0 or 1;

n is an integer selected from 1 to 4;

10 X¹, X², X³, X⁴ and X⁵ are independently absent or selected from the group consisting of a bond, H, halogen, CN, R¹, OR¹ or SR¹;

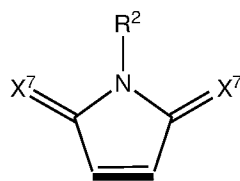
15 wherein R¹ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A¹ is selected from the group consisting of O, S, Se, Te, C and N

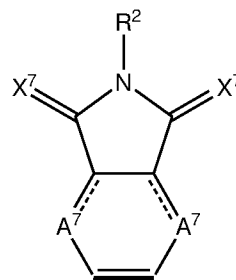
A², A³, A⁴, A⁵ and A⁶ are independently C or N; and

20 wherein any two substituents selected from the group consisting of X¹, X², X³, X⁴ and X⁵ may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.;

P² has the following formula (IIIa) or (IIIb);



(IIIa)



(IIIb)

wherein

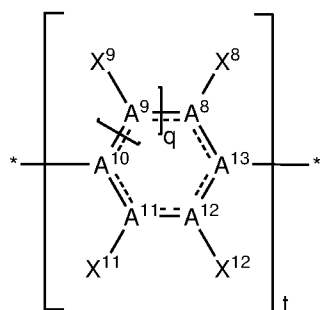
R² is an optionally substituted alkyl or optionally substituted aryl;

X⁷ is O or S;

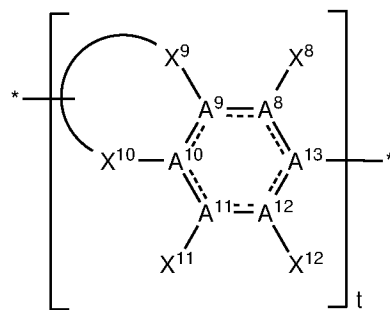
A⁷ is CH, CH₂ or N;

and — is where the compound of Formula (IIIa) or (IIIb) is fused to the compound of Formula (IV);

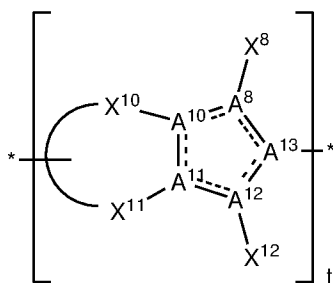
P³ has the following Formula (Va), (Vb) or (Vc) ;



(Va)



(Vb)



(Vc)

wherein

q is 0 or 1;

t is an integer selected from 1 to 4;

X⁸, X⁹, X¹¹ and X¹² are independently absent or selected from the group consisting of a bond, H, halogen, CN, R³, OR³ or SR³;

wherein R^3 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

5 A^8 is selected from the group consisting of O, S, Se, Te, C and N

A^9 , A^{10} , A^{11} , A^{12} and A^{13} are independently C or N;

wherein any two substituents selected from the group consisting of X^8 , X^9 , X^{10} , X^{11} and X^{12} may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

and P^4 is absent, or an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl. a is any value from 0 to 1; and

b is an integer selected from 1 to 10,000; and

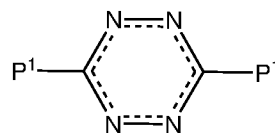
y is an integer selected from 0 to 5.

Advantageously, the compound of Formula (IV) may be a polymer. The purification of a polymer may be much easier and more convenient than purification of small molecules. Advantageously, the simple purification process may significantly reduce the cost of production of the polymer. Further advantageously, the polymer may have good solubility in a variety of solvents. The polymer may be soluble in non-chlorinated solvents, making the polymer easily processable in solution. This may further reduce the cost of production. More advantageously, the polymer may become glassy upon heating and this may be useful in manufacturing devices using the polymer material.

Further advantageously, the polymer may be a donor-acceptor polymer. Advantageously, the polymer may be comprised of donor compounds and acceptor compounds. Further advantageously, the donor compounds and acceptor compounds may be selected to confer advantageous properties to the polymer. Advantageously, the acceptor compound in the polymer may be the compound of Formula (I) as defined above. The ultra-electron deficient nature of the compound of Formula (I) as defined above may enable ease of synthesis of the polymer as well as confer advantageous properties to the polymer. Further advantageously, the pyridazine or phthalazine group of the compound of Formula (I) may lower the frontier orbitals of the polymers to make the polymer more stable under ambient conditions.

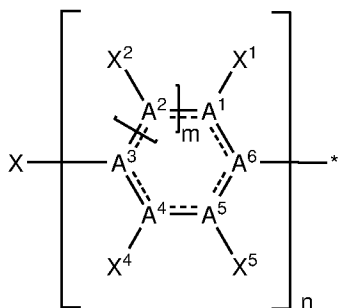
The performance of donor-acceptor type conjugated oligomers and polymers may rely on many factors, including the identity of the donor and acceptor building block of the polymer, the polymerization strategy and the molar weight of the polymer. Advantageously, the compound of Formula (IV) as defined above has been synthesized by judicious choice of the donor and acceptor building block, polymerization strategy and molecular weight of the polymer to so that the polymer has the advantageous properties such as good band-gap, good optical property, high stability and low cost of production.

In a third aspect, there is provided a compound having the following Formula (VI);

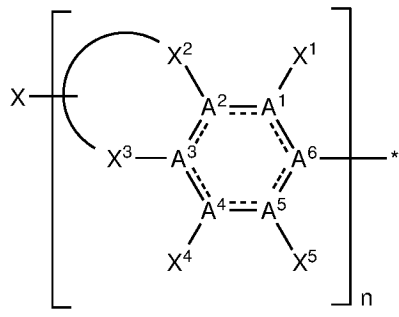


(VI)

wherein P¹ has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

wherein

----- is a single or double bond, as valency allows;

m is 0 or 1;

n is an integer selected from 1 to 4;

10 X, X¹, X², X³, X⁴ and X⁵ are independently absent or selected from the group consisting of a bond, H, halogen, CN, R¹, OR¹ or SR¹;

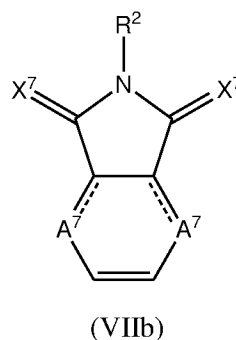
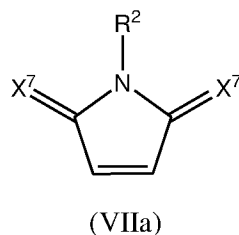
wherein R¹ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A¹ is selected from the group consisting of O, S, Se, Te, C and N;

20 A², A³, A⁴, A⁵ and A⁶ are independently C or N; and wherein any two substituents selected from the group consisting of X¹, X², X³, X⁴ and X⁵ may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

Advantageously, the compound of Formula (I) as defined above may be a useful starting material for the synthesis of compounds defined further below. Advantageously, the compound of Formula (I) as defined above may comprise a tetrazine moiety attached to two electron donating groups. Advantageously, the tetrazine moiety may be electron-rich, such that when reacted with a dienophile defined further below, the resulting product will have ultra-high electron affinity.

In a fourth aspect, there is provided a compound having the following formula (VIIa) or (VIIb);



wherein

----- is a single or double bond, as valency allows;

5 R^2 is an optionally substituted alkyl or optionally substituted aryl;

X^7 is O or S; and

A^7 is CH, CH_2 or N.

Advantageously, the compounds of formula (VIIa) or (VIIb) as defined above may be intrinsically electron-withdrawing, such that when reacted with the tetrazine compound having Formula (VI) as defined above, the resulting product will have ultra-high electron affinity. Further advantageously, the compounds of Formula (VIIa) or (VIIb) may be easy to functionalize. More advantageously, the compound of Formula (VIIa) or (VIIb) as defined above may be tunable by their R^2 functional group to enhance their solubility properties such that they may be useful in reactions performed in a variety of solvents.

15 In a fifth aspect, there is provided a method for synthesizing the compound of Formula (VI) as defined above, comprising the steps of providing a hydrazine and contacting the hydrazine with a functionalized cyclic group, wherein the cyclic group of the functionalized cyclic group is selected from the group comprising of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted tellurophene, optionally substituted pyrrole, optionally substituted phenylene, optionally substituted aza-phenylene, optionally substituted arylene diimide, optionally substituted fluorene, optionally substituted cabazole, optionally substituted dibenzodilole, optionally substituted benzooxodiazole, optionally substituted benzotriazole, optionally substituted benzothidiazole and any combination thereof.

25 In a sixth aspect, there is provided a method for synthesizing the compound of Formula (I) as defined above, comprising the steps of:

providing the compound of Formula (VI) of claim 3; and

contacting the compound of Formula (VI) of claim 3 with the compound of Formulae (VIIa) or (VIIb) of claim 4 under reaction conditions to form the compound of Formula (I) of claim 1.

Advantageously, the method for synthesizing the compound of Formula (I) as defined above may be an inverse-electron demanding Diels-Alder reaction. Conventionally, for Diels-Alder reactions that are being carried out on a tetrazine, the tetrazine acts as a diene and therefore should be modified with electron withdrawing groups to enhance its reactivity. Conversely, the dienophile should be modified with electron donating groups. This is to facilitate the inverse electron demanding Diels-Alder

reaction. However, in the synthesis of the compound of Formula (I) as defined above, the tetrazine moiety has two electron donating units P1 attached. In addition, the dienophile (compounds of Formulae (VIIa) or (VIIb) as defined above) is an intrinsically electron withdrawing imide. Under such conditions, the inverse-electron demanding Diels-Alder reaction has conventionally faced challenges due to the unfavourable electronic interaction between the tetrazine and the dienophile.

However, advantageously, the compound of Formula (I) may be synthesized with a good overall yield by the method as defined above. More advantageously, the successful synthesis may be due to judicious choice of reaction solvents, reaction temperature and reaction duration. Advantageously, the solvent used for the reaction may not contain any reactivity towards the reaction mixture. More advantageously, the boiling point of the solvent may be sufficiently high to allow the reaction to proceed. Advantageously, the method as defined above may enable the synthesis of the compound of Formula (I) with an isolated yield of higher than 90%.

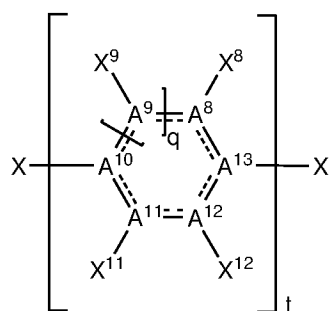
Further advantageously, the method as defined above is scalable. The compound of Formula (I) as defined above may therefore be synthesized at a larger scale of up to 500 g.

In an seventh aspect, there is provided a method for synthesizing the compound of Formula (IV) as defined above, comprising the step of:

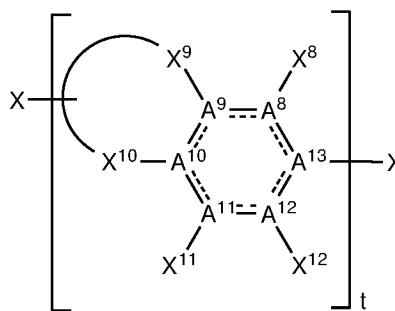
providing the compound of Formula (I) of claim 1; and

contacting the compound of Formula (I) of claim 1 with;

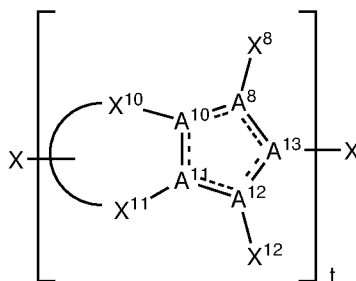
(i) a compound having the following Formula (XXVa), (XXVb) or (XXVc) ;



(XXVa)



(XXVb)



(XXVc)

wherein

----- is a single or double bond, as valency allows;

q is 0 or 1;

t is an integer selected from 1 to 4;

X, X⁸, X⁹, X¹¹ and X¹² are independently absent or selected from the group consisting of a bond, H, halogen, CN, R³, OR³ or SR³;

5 wherein R³ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A⁸ is selected from the group consisting of O, S, Se, Te, C and N

A⁹, A¹⁰, A¹¹, A¹² and A¹³ are independently C or N; and

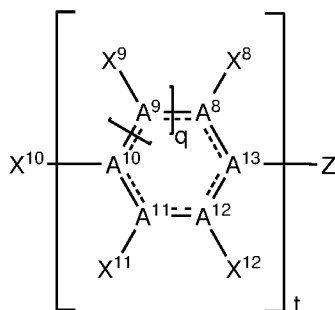
10 wherein any two substituents selected from the group consisting of X⁸, X⁹, X¹⁰, X¹¹ and X¹² may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl; and

15 (ii) a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group is selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

20 in the presence of a metal-containing catalyst.

In an eighth aspect, there is provided a method for synthesizing the compound of Formula (IV) as defined above, comprising the steps of:

1) providing the compound of Formula (I) of claim 1; and
 2) contacting the compound of Formula (I) of claim 1 with a compound having the
 25 following Formula (XXVI);



(XXVI)

wherein

==== is a single or double bond, as valency allows;

30 q is 0 or 1;

t is an integer selected from 1 to 4;

Z is a functional group containing zinc, tin or born;

X^8 , X^9 , X^{10} , X^{11} and X^{12} are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^3 , OR^3 or SR^3 ;

wherein R^3 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A^8 is selected from the group consisting of O, S, Se, Te, C and N

A^9 , A^{10} , A^{11} , A^{12} and A^{13} are independently C or N; and

wherein any two substituents selected from the group consisting of X^8 , X^9 , X^{10} , X^{11} and X^{12} may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

in the presence of a metal-containing catalyst to form a monomer precursor;

3) reacting the monomer precursor of step (2) with N-bromosuccinimide to form a reactive monomer; and

4) reacting the reactive monomer of step (2) with a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group is selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

in the presence of a metal-containing catalyst.

Advantageously, the method as defined above may have a high yield of synthesis. Further advantageously, the method as defined above may facilitate a controlled polymerization of the monomers, giving rise to polymers with defined ratios of donors and acceptors.

In a ninth aspect, there is provided the use of the compound of Formula (IV) as defined above, in the manufacture of semiconductor devices.

In a tenth aspect, there is provided a semiconductor device comprising the compound of Formula (IV) as defined above.

Advantageously, the compound of Formula (IV) as defined above may be useful in the manufacture of semiconductor devices. More advantageously, the compound of Formula (IV) as defined above may have enhanced processability, enabling them to be used in the manufacture of more processable polymers. Advantageously, the semiconductor devices manufactured using the compound of Formula (IV) as defined above may be used in a wide range of applications such as electrochromic materials, organic light-emitting diode, organic thin-film transistors and organic photovoltaic cells. Advantageously, the semiconductor devices manufactured using the compound of Formula (IV) may have higher stability, long shelf-life, high performance and may be cheaper to manufacture. Further

advantageously, the device comprising the compound of Formula (IV) as defined above may have improved optical properties.

Definitions

In this specification a number of terms are used which are well known to a skilled addressee. Nevertheless for the purposes of clarity a number of terms will be defined. The following words and terms used herein shall have the meaning indicated:

In the definitions of a number of substituents below it is stated that "the group may be a terminal group or a bridging group". This is intended to signify that the use of the term is intended to encompass the situation where the group is a linker between two other portions of the molecule as well as where it is a terminal moiety. Using the term alkyl as an example, some publications would use the term "alkylene" for a bridging group and hence in these other publications there is a distinction between the terms "alkyl" (terminal group) and "alkylene" (bridging group). In the present application no such distinction is made and most groups may be either a bridging group or a terminal group.

"Acyl" means an R-C(=O)- group in which the R group may be an alkyl, cycloalkyl, heterocycloalkyl, aryl or heteroaryl group as defined herein. Examples of acyl include acetyl and benzoyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

"Acylamino" means an R-C(=O)-NH- group in which the R group may be an alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

"Alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched preferably having 2-12 carbon atoms, more preferably 2-10 carbon atoms, most preferably 2-6 carbon atoms, in the normal chain. The group may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. Exemplary alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and nonenyl. The group may be a terminal group or a bridging group.

"Alkenyloxy" refers to an alkenyl-O- group in which alkenyl is as defined herein. Preferred alkenyloxy groups are C₁-C₆ alkenyloxy groups. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Alkyl" as a group or part of a group refers to a linear or branched aliphatic hydrocarbon group, preferably a C₁-C₂₅ alkyl, more preferably a C₁-C₁₀ alkyl, most preferably C₁-C₆ unless otherwise noted. Examples of suitable straight and branched C₁-C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

"Alkylamino" includes both mono-alkylamino and dialkylamino, unless specified. "Mono-alkylamino" means a Alkyl-NH- group, in which alkyl is as defined herein. "Dialkylamino" means a

(alkyl)₂N- group, in which each alkyl may be the same or different and are each as defined herein for alkyl. The alkyl group is preferably a C₁-C₆ alkyl group. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

5 "Alkylaminocarbonyl" refers to a group of the formula (Alkyl)_x(H)_yNC(=O)- in which alkyl is as defined herein, x is 1 or 2, and the sum of X+Y =2. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

10 "Alkyloxy" refers to an alkyl-O- group in which alkyl is as defined herein. Preferably the alkyloxy is a C₁-C₆alkyloxy. Examples include, but are not limited to, methoxy and ethoxy. The group may be a terminal group or a bridging group.

"Alkyloxyalkyl" refers to an alkyloxy-alkyl- group in which the alkyloxy and alkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

15 "Alkyloxyary" refers to an alkyloxy-aryl- group in which the alkyloxy and aryl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the aryl group.

20 "Alkyloxycarbonyl" refers to an alkyl-O-C(=O)- group in which alkyl is as defined herein. The alkyl group is preferably a C₁-C₆ alkyl group. Examples include, but are not limited to, methoxycarbonyl and ethoxycarbonyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

25 "Alkyloxycycloalkyl" refers to an alkyloxy-cycloalkyl- group in which the alkyloxy and cycloalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the cycloalkyl group.

"Alkyloxyheteroaryl" refers to an alkyloxy-heteroaryl- group in which the alkyloxy and heteroaryl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroaryl group.

30 "Alkyloxyheterocycloalkyl" refers to an alkyloxy-heterocycloalkyl- group in which the alkyloxy and heterocycloalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heterocycloalkyl group.

35 "Alkylsulfinyl" means an alkyl-S(=O)- group in which alkyl is as defined herein. The alkyl group is preferably a C₁-C₆ alkyl group. Exemplary alkylsulfinyl groups include, but not limited to, methylsulfinyl and ethylsulfinyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

"Alkylsulfonyl" refers to an alkyl-S(=O)₂- group in which alkyl is as defined above. The alkyl group is preferably a C₁-C₆ alkyl group. Examples include, but not limited to methylsulfonyl

and ethylsulfonyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

"Alkynyl" as a group or part of a group means an aliphatic hydrocarbon group containing a carbon-carbon triple bond and which may be straight or branched preferably having from 2-12 carbon atoms, more preferably 2-10 carbon atoms, more preferably 2-6 carbon atoms in the normal chain. Exemplary structures include, but are not limited to, ethynyl and propynyl. The group may be a terminal group or a bridging group.

"Alkynyloxy" refers to an alkynyl-O- group in which alkynyl is as defined herein. Preferred alkynyloxy groups are C₁-C₆ alkynyloxy groups. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Amino" refers to groups of the form -NR_aR_b wherein R_a and R_b are individually selected from the group including but not limited to hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, and optionally substituted aryl groups.

"Aminoalkyl" means an NH₂-alkyl- group in which the alkyl group is as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

"Aminosulfonyl" means an NH₂-S(=O)₂- group. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

"Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 18 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C₅₋₇ cycloalkyl or C₅₋₇ cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C₃-C₁₈ aryl group.

"Arylalkenyl" means an aryl-alkenyl- group in which the aryl and alkenyl are as defined herein. Exemplary arylalkenyl groups include phenylallyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

"Arylalkyl" means an aryl-alkyl- group in which the aryl and alkyl moieties are as defined herein. Preferred arylalkyl groups contain a C₁₋₅ alkyl moiety. Exemplary arylalkyl groups include benzyl, phenethyl, 1-naphthalenemethyl and 2-naphthalenemethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

"Arylalkyloxy" refers to an aryl-alkyl-O- group in which the alkyl and aryl are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Arylamino" includes both mono-arylamino and di-arylamino unless specified. Mono-arylamino means a group of formula arylNH- , in which aryl is as defined herein. di-arylamino means a group of formula $(\text{aryl})_2\text{N-}$ where each aryl may be the same or different and are each as defined herein for aryl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

"Arylheteroalkyl" means an aryl-heteroalkyl- group in which the aryl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

"Aryloxy" refers to an aryl-O- group in which the aryl is as defined herein. Preferably the aryloxy is a $\text{C}_6\text{-C}_{18}$ aryloxy, more preferably a $\text{C}_6\text{-C}_{10}$ aryloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Arylsulfonyl" means an aryl-S(=O)₂- group in which the aryl group is as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

A "bond" is a linkage between atoms in a compound or molecule. The bond may be a single bond, a double bond, or a triple bond.

"Cycloalkenyl" means a non-aromatic monocyclic or multicyclic ring system containing at least one carbon-carbon double bond and preferably having from 5-10 carbon atoms per ring. Exemplary monocyclic cycloalkenyl rings include cyclopentenyl, cyclohexenyl or cycloheptenyl. The cycloalkenyl group may be substituted by one or more substituent groups. A cycloalkenyl group typically is a $\text{C}_3\text{-C}_{12}$ alkenyl group. The group may be a terminal group or a bridging group.

"Cycloalkyl" refers to a saturated monocyclic or fused or spiro polycyclic, carbocycle preferably containing from 3 to 9 carbons per ring, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like, unless otherwise specified. It includes monocyclic systems such as cyclopropyl and cyclohexyl, bicyclic systems such as decalin, and polycyclic systems such as adamantane. A cycloalkyl group typically is a $\text{C}_3\text{-C}_{12}$ alkyl group. The group may be a terminal group or a bridging group.

"Cycloalkylalkyl" means a cycloalkyl-alkyl- group in which the cycloalkyl and alkyl moieties are as defined herein. Exemplary monocycloalkylalkyl groups include cyclopropylmethyl, cyclopentylmethyl, cyclohexylmethyl and cycloheptylmethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

"Cycloalkylalkenyl" means a cycloalkyl-alkenyl- group in which the cycloalkyl and alkenyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

"Cycloalkylheteroalkyl" means a cycloalkyl-heteroalkyl- group in which the cycloalkyl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

"Cycloalkyloxy" refers to a cycloalkyl-O- group in which cycloalkyl is as defined herein. Preferably the cycloalkyloxy is a C₁-C₆cycloalkyloxy. Examples include, but are not limited to, cyclopropanoxy and cyclobutanoxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

5 "Cycloalkenyloxy" refers to a cycloalkenyl-O- group in which the cycloalkenyl is as defined herein. Preferably the cycloalkenyloxy is a C₁-C₆cycloalkenyloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

10 "Cycloamino" refers to a saturated monocyclic, bicyclic, or polycyclic ring containing at least one nitrogen in at least one ring. Each ring is preferably from 3 to 10 membered, more preferably 4 to 7 membered. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

15 "Haloalkyl" refers to an alkyl group as defined herein in which one or more of the hydrogen atoms has been replaced with a halogen atom selected from the group consisting of fluorine, chlorine, bromine and iodine. A haloalkyl group typically has the formula C_nH_(2n+1-m)X_m wherein each X is independently selected from the group consisting of F, Cl, Br and I. In groups of this type n is typically from 1 to 10, more preferably from 1 to 6, most preferably 1 to 3. m is typically 1 to 6, more preferably 1 to 3. Examples of haloalkyl include fluoromethyl, difluoromethyl and trifluoromethyl.

20 "Haloalkenyl" refers to an alkenyl group as defined herein in which one or more of the hydrogen atoms has been replaced with a halogen atom independently selected from the group consisting of F, Cl, Br and I.

"Haloalkynyl" refers to an alkynyl group as defined herein in which one or more of the hydrogen atoms has been replaced with a halogen atom independently selected from the group consisting of F, Cl, Br and I.

25 "Halogen" represents chlorine, fluorine, bromine or iodine.

30 "Heteroalkyl" refers to a straight- or branched-chain alkyl group preferably having from 2 to 12 carbons, more preferably 2 to 6 carbons in the chain, one or more of which has been replaced by a heteroatom selected from S, O, P and N. Exemplary heteroalkyls include alkyl ethers, secondary and tertiary alkyl amines, amides, alkyl sulfides, and the like. Examples of heteroalkyl also include hydroxyC₁-C₆alkyl, C₁-C₆alkyloxyC₁-C₆alkyl, aminoC₁-C₆alkyl, C₁-C₆alkylaminoC₁-C₆alkyl, and di(C₁-C₆alkyl)aminoC₁-C₆alkyl. The group may be a terminal group or a bridging group.

"Heteroalkyloxy" refers to a heteroalkyl-O- group in which heteroalkyl is as defined herein. Preferably the heteroalkyloxy is a C₁-C₆heteroalkyloxy. The group may be a terminal group or a bridging group.

35 "Heteroaryl" either alone or part of a group refers to groups containing an aromatic ring (preferably a 5 or 6 membered aromatic ring) having one or more heteroatoms as ring atoms in the aromatic ring with the remainder of the ring atoms being carbon atoms. Suitable heteroatoms include nitrogen, oxygen and sulphur. Examples of heteroaryl include thiophene, benzothiophene, benzofuran, benzimidazole, benzoxazole, benzothiazole, benzisothiazole, naphtho[2,3-b]thiophene, 40 furan, isoindolizine, xantholene, phenoxatine, pyrrole, imidazole, pyrazole, pyridine, pyrazine,

pyrimidine, pyridazine, tetrazole, indole, isoindole, 1H-indazole, purine, quinoline, isoquinoline, phthalazine, naphthyridine, quinoxaline, cinnoline, carbazole, phenanthridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole, isooxazole, furazane, phenoxazine, 2-, 3- or 4- pyridyl, 2-, 3-, 4-, 5-, or 8- quinolyl, 1-, 3-, 4-, or 5- isoquinolyl, 1-, 2-, or 3- indolyl, and 2-, or 3-thienyl. A heteroaryl group is typically a C₁-C₁₈ heteroaryl group. The group may be a terminal group or a bridging group. Typically a heteroaryl group is a 3 to 18 membered group.

"Heteroarylalkyl" means a heteroaryl-alkyl group in which the heteroaryl and alkyl moieties are as defined herein. Preferred heteroarylalkyl groups contain a lower alkyl moiety. Exemplary heteroarylalkyl groups include pyridylmethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

"Heteroarylalkenyl" means a heteroaryl-alkenyl- group in which the heteroaryl and alkenyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

"Heteroarylheteroalkyl" means a heteroaryl-heteroalkyl- group in which the heteroaryl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

"Heteroarylamino" refers to groups containing an aromatic ring (preferably 5 or 6 membered aromatic ring) having at least one nitrogen and at least another heteroatom as ring atoms in the aromatic ring, preferably from 1 to 3 heteroatoms in at least one ring. Suitable heteroatoms include nitrogen, oxygen and sulphur. Arylamino and aryl is as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

"Heteroaryloxy" refers to a heteroaryl-O- group in which the heteroaryl is as defined herein. Preferably the heteroaryloxy is a C₁-C₁₈heteroaryloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Heterocyclic" refers to saturated, partially unsaturated or fully unsaturated monocyclic, bicyclic or polycyclic ring system containing at least one heteroatom selected from the group consisting of nitrogen, sulfur and oxygen as a ring atom. Examples of heterocyclic moieties include heterocycloalkyl, heterocycloalkenyl and heteroaryl.

"Heterocycloalkenyl" refers to a heterocycloalkyl as defined herein but containing at least one double bond. A heterocycloalkenyl group typically is a C₂-C₁₂ heterocycloalkenyl group. The group may be a terminal group or a bridging group.

"Heterocycloalkyl" refers to a saturated monocyclic, bicyclic, or polycyclic ring containing at least one heteroatom selected from nitrogen, sulfur, oxygen, preferably from 1 to 3 heteroatoms in at least one ring. Each ring is preferably from 3 to 10 membered, more preferably 4 to 7 membered. Examples of suitable heterocycloalkyl substituents include pyrrolidyl, tetrahydrofuryl, tetrahydrothiofuryl, piperidyl, piperazyl, tetrahydropyranlyl, morpholino, 1,3-diazapane, 1,4-

diazapane, 1,4-oxazepane, and 1,4-oxathiapane. A heterocycloalkyl group typically is a C₂-C₁₂ heterocycloalkyl group. The group may be a terminal group or a bridging group.

"Heterocycloalkylalkyl" refers to a heterocycloalkyl-alkyl- group in which the heterocycloalkyl and alkyl moieties are as defined herein. Exemplary heterocycloalkylalkyl groups include (2-tetrahydrofuryl)methyl, (2-tetrahydrothiofuranyl) methyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl group.

"Heterocycloalkylalkenyl" refers to a heterocycloalkyl-alkenyl- group in which the heterocycloalkyl and alkenyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkenyl group.

"Heterocycloalkylheteroalkyl" means a heterocycloalkyl-heteroalkyl- group in which the heterocycloalkyl and heteroalkyl moieties are as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the heteroalkyl group.

"Heterocycloalkyloxy" refers to a heterocycloalkyl-O- group in which the heterocycloalkyl is as defined herein. Preferably the heterocycloalkyloxy is a C₁-C₆heterocycloalkyloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Heterocycloalkenyloxy" refers to a heterocycloalkenyl-O- group in which heterocycloalkenyl is as defined herein. Preferably the Heterocycloalkenyloxy is a C₁-C₆ Heterocycloalkenyloxy. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the oxygen atom.

"Heterocycloamino" refers to a saturated monocyclic, bicyclic, or polycyclic ring containing at least one nitrogen and at least another heteroatom selected from nitrogen, sulfur, oxygen, preferably from 1 to 3 heteroatoms in at least one ring. Each ring is preferably from 3 to 10 membered, more preferably 4 to 7 membered. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

"Hydroxyalkyl" refers to an alkyl group as defined herein in which one or more of the hydrogen atoms has been replaced with an OH group. A hydroxyalkyl group typically has the formula C_nH_(2n+1-x)(OH)_x. In groups of this type n is typically from 1 to 10, more preferably from 1 to 6, most preferably from 1 to 3. x is typically from 1 to 6, more preferably from 1 to 4.

"Lower alkyl" as a group means unless otherwise specified, an aliphatic hydrocarbon group which may be straight or branched having 1 to 6 carbon atoms in the chain, more preferably 1 to 4 carbons such as methyl, ethyl, propyl (n-propyl or isopropyl) or butyl (n-butyl, isobutyl or tertiary-butyl). The group may be a terminal group or a bridging group.

"Subject" refers to a human or an animal.

"Sulfinyl" means an R-S(=O)- group in which the R group may be OH, alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a

bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

"Sulfinylamino" means an R-S(=O)-NH- group in which the R group may be OH, alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

"Sulfonyl" means an R-S(=O)₂- group in which the R group may be OH, alkyl, cycloalkyl, heterocycloalkyl; aryl or heteroaryl group as defined herein. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the sulfur atom.

"Sulfonylamino" means an R-S(=O)₂-NH- group. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the nitrogen atom.

It is understood that included in the family of compounds of Formula (I) are isomeric forms including diastereoisomers, enantiomers, tautomers, and geometrical isomers in "E" or "Z" configurational isomer or a mixture of E and Z isomers. It is also understood that some isomeric forms such as diastereomers, enantiomers, and geometrical isomers can be separated by physical and/or chemical methods and by those skilled in the art.

Some of the compounds of the disclosed embodiments may exist as single stereoisomers, racemates, and/or mixtures of enantiomers and /or diastereomers. All such single stereoisomers, racemates and mixtures thereof, are intended to be within the scope of the subject matter described and claimed.

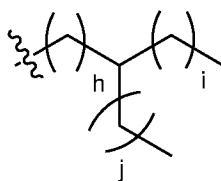
Additionally, Formula (I) is intended to cover, where applicable, solvated as well as unsolvated forms of the compounds. Thus, each formula includes compounds having the indicated structure, including the hydrated as well as the non-hydrated forms.

Further, it is possible that compounds of the invention may contain more than one asymmetric carbon atom. In those compounds, the use of a solid line to depict bonds to asymmetric carbon atoms is meant to indicate that all possible stereoisomers are meant to be included. The use of a solid line to depict bonds to one or more asymmetric carbon atoms in a compound of the invention and the use of a solid or dotted wedge to depict bonds to other asymmetric carbon atoms in the same compound is meant to indicate that a mixture of diastereomers is present.

The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups independently selected from alkyl, alkenyl, alkynyl, thioalkyl, cycloalkyl, cycloalkylalkyl, cycloalkenyl, cycloalkylalkenyl, heterocycloalkyl, cycloalkylheteroalkyl, cycloalkyloxy, cycloalkenyloxy, cycloamino, halo, carboxyl, haloalkyl, haloalkynyl, alkynyloxy, heteroalkyl, heteroalkyloxy, hydroxyl, hydroxyalkyl, alkoxy, thioalkoxy, alkenyloxy, haloalkoxy, haloalkenyl, haloalkynyl, haloalkenyloxy, nitro, amino, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroheterocyclyl, alkylamino, dialkylamino, alkenylamine, aminoalkyl, alkynylamino, acyl, alkyloxy, alkyloxyalkyl, alkyloxyaryl, alkyloxycarbonyl, alkyloxcycloalkyl, alkyloxyheteroaryl, alkyloxyheterocycloalkyl, alkenoyl, alkynoyl, acylamino, diacylamino, acyloxy, alkylsulfonyloxy, heterocyclic, heterocycloalkenyl, heterocycloalkyl,

heterocycloalkylalkyl, heterocycloalkylalkenyl, heterocycloalkylheteroalkyl, heterocycloalkyloxy, heterocycloalkenyloxy, heterocycloxy, heterocycloamino, haloheterocycloalkyl, alkylsulfinyl, alkylsulfonyl, alkylsulfenyl, alkylcarbonyloxy, alkylthio, acylthio, aminosulfonyl, phosphorus-containing groups such as phosphono and phosphinyl, sulfinyl, sulfinylamino, sulfonyl, sulfonylamino, aryl, heteroaryl, heteroarylalkyl, heteroarylalkenyl, heteroarylheteroalkyl, heteroarylamino, heteroaryloxy, arylalkenyl, arylalkyl, alkylaryl, alkylheteroaryl, aryloxy, arylsulfonyl, cyano, cyanate, isocyanate, $-C(O)NH(alkyl)$, and $-C(O)N(alkyl)_2$.

The term "optionally substituted alkyl", for the purpose of this application, refers to an optionally substituted linear alkyl or an optionally substituted branched alkyl. The optionally substituted linear alkyl may be an optionally substituted C_1 to C_{25} linear alkyl. The optionally substituted branched alkyl may be an optionally substituted C_1 to C_{25} branched alkyl. The optionally substituted branched alkyl may have the following formula (A), where h may be 0 or 1. i and j may independently be integers selected from 1 to 13. h may be 1. i may be 7. j may be 9.



(A).

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of

the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

5 Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig.1

10 [Fig. 1] is a representative scheme for the synthesis of the polymer 1, polymer 2 and polymer 3.

Fig.2

[Fig 2] shows the GPC curve and the reading of polymer 1.

Fig.3

[Fig 3] shows the GPC curve and the reading of polymer 2.

15 Fig.4

[Fig 4] shows the GPC curve and the reading of polymer 3.

Fig.5

[Fig. 5] are UV-visible spectra of solutions of the polymer 1, polymer 2 and polymer 3 in chlorobenzene and thin films.

20 Fig.6

[Fig. 6] is a schematic drawing of the polymer device.

Fig.7

[Fig. 7] is a UV-vis-NIR spectrum of a polymer 1 device at various applied potentials (V). (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.5, (e) 0.6, (f) 0.7, (g) 0.8, (h) 0.9, (i) 1.0, (j) 1.1, (k) 1.2, (l) 1.3, (m) 1.4,
25 (n) 1.5, (o) 1.6, (p) 1.7, (q) 1.8 V.

Fig.8

[Fig. 8] is a UV-vis-NIR spectrum of a polymer 2 device at various applied potentials (V). (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.5, (e) 0.6, (f) 0.7, (g) 0.8, (h) 0.9, (i) 1.0, (j) 1.1, (k) 1.2, (l) 1.3, (m) 1.4, (n) 1.5, (o) 1.6, (p) 1.7, (q) 1.8 V.

Fig.9

[Fig. 9] is a UV-vis-NIR spectrum of a polymer 3 device at various applied potentials (V). (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.5, (e) 0.6, (f) 0.7, (g) 0.8, (h) 0.9, (i) 1.0, (j) 1.1, (k) 1.2, (l) 1.3, (m) 1.4, (n) 1.5, (o) 1.6, (p) 1.7, (q) 1.8 V.

5 Fig.10

[Fig. 10] is a square-wave potential step absorptiometry spectrum of a polymer 1 device between 1.5 V and -1.5 V with a switch time of 10 seconds.

Fig.11

10 [Fig. 11] is a square-wave potential step absorptiometry spectrum of a polymer 2 device between 1.5 V and -1.5 V with a switch time of 10 seconds.

Fig.12

[Fig. 12] is a square-wave potential step absorptiometry spectrum of a polymer 3 device between 1.5 V and -1.5 V with a switch time of 10 seconds.

Fig.13

15 [Fig. 13] are photos of polymers 1, polymer 2 and polymer 3 (from left to right) devices in their neutral (top) and 2.0 V (bottom) states.

Fig.14

[Fig. 14] is a representative scheme for the synthesis of the polymer 4, polymer 5 and polymer 6.

Fig.15

20 [Fig. 15] is a ^1H -NMR spectrum of a synthesized compound, recorded in CDCl_3 .

Fig.16

[Fig. 16] is a ^{13}C -NMR spectrum of a synthesized intermediate, recorded in CDCl_3 .

Fig.17

[Fig. 17] is a HRMS spectrum of a synthesized intermediate.

25 Fig.18

[Fig. 18] is a ^1H -NMR spectrum of the synthesized polymer 4, recorded in CDCl_3 .

Fig.19

[Fig. 19] is a ^1H -NMR spectrum of the synthesized polymer 5, recorded in CDCl_3 .

Fig.20

30 [Fig. 20] is a ^1H -NMR spectrum of the synthesized polymer 6, recorded in CDCl_3 .

Fig.21

[Fig. 21] is a EC electrospectroscopy of polymer 5 in a EC device.

Fig.22

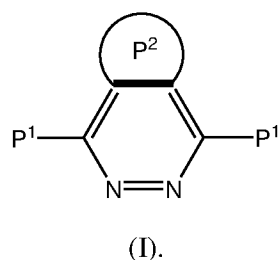
[Fig. 22] is a Time-dependent density-functional theory calculation, carried out to compare the magnitude of electron deficiency of the imide-fused pyridazines with current commonly used electron deficient acceptors.

Fig.23

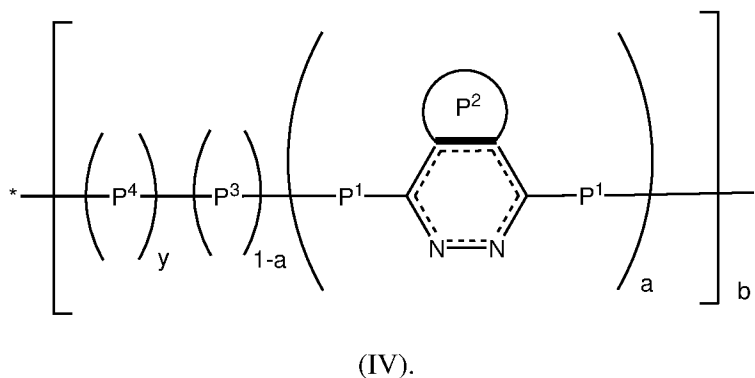
[Fig. 23] is a HR-EI MS spectrum of a synthesized intermediate.

Detailed Description of Embodiments

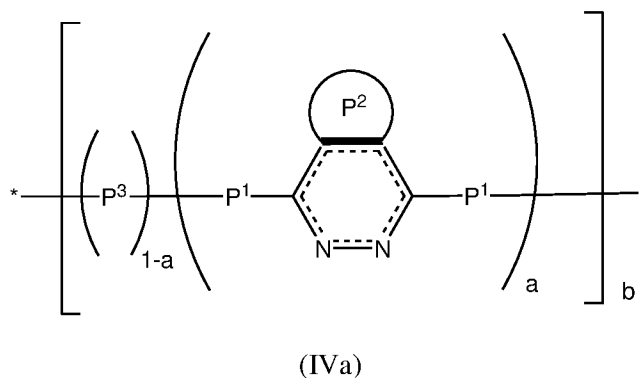
10 A compound may have the following Formula (I);

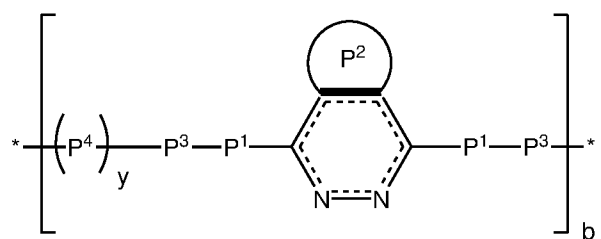


A compound may have repeating units of the following Formula (IV);



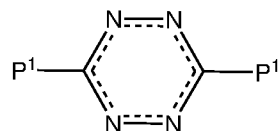
A compound may have repeating units of the following formula (IVa) or (IVb):





(IVb).

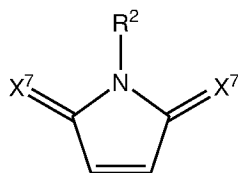
A compound may have the following Formula (VI);



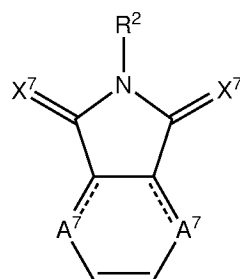
(VI).

5

A compound may have the following formula (VIIa) or (VIIb);

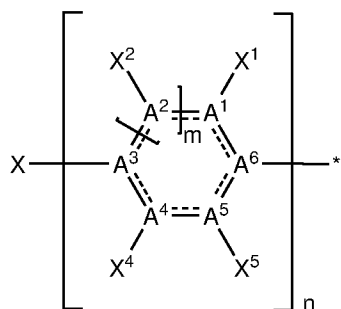


(VIIa)

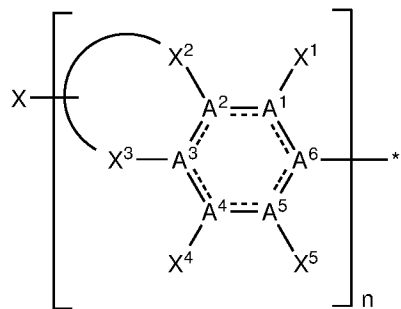


(VIIb).

10 P¹ may have the following Formula (IIa) or (IIb);

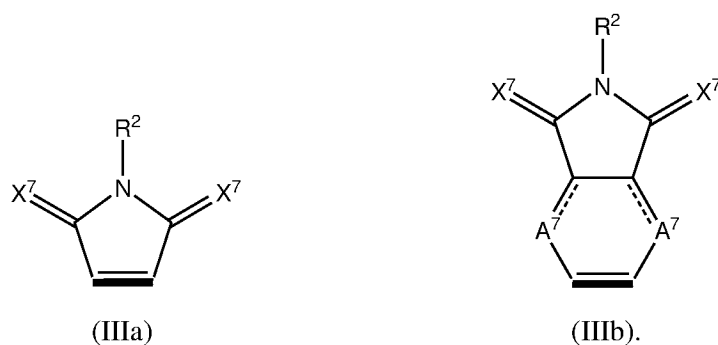


(IIa)

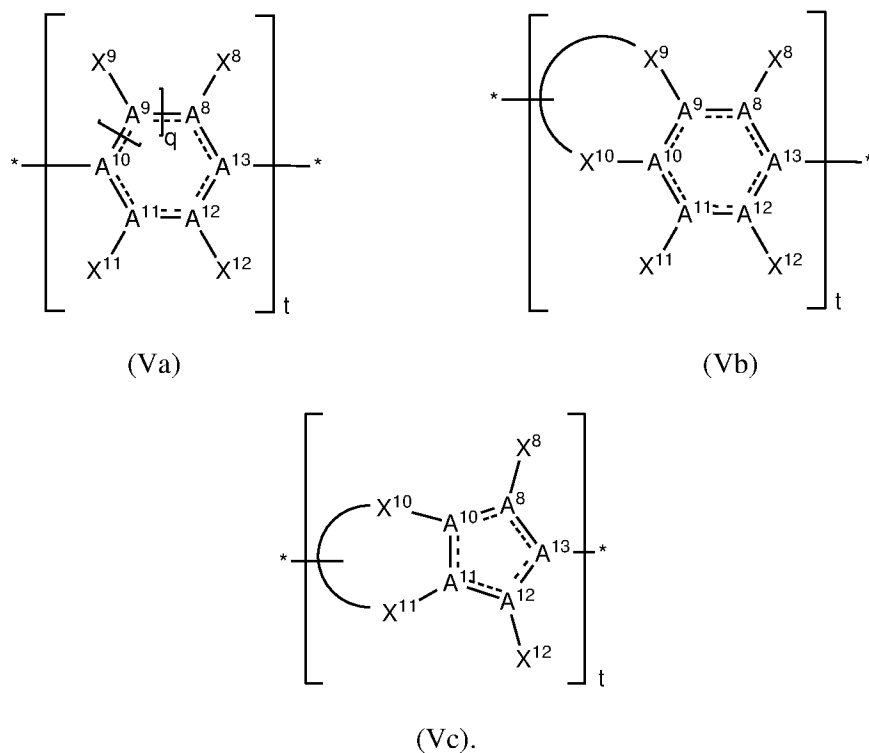


(IIb).

P² may have the following formula (IIIa) or (IIIb);



P³ has the following Formula (Va), (Vb) or (Vc);



P⁴ may be absent, or an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

----- may be a single or double bond, as valency allows.

m may be 0 or 1.

n may be an integer selected from 1 to 4.

X, X¹, X², X³, X⁴ and X⁵ may independently be absent or selected from the group consisting of a bond, H, halogen, CN, R¹, OR¹ or SR¹.

Halogen may be selected from the group consisting of F, Cl, Br and I.

X may be selected from the group consisting of halogen, CN, R¹ and OR¹.

R¹ may be selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl. R¹ may be an optionally substituted alkyl.

5 A¹ may be selected from the group consisting of O, S, Se, Te, C and N.

A², A³, A⁴, A⁵ and A⁶ may independently be C or N.

Any two substituents selected from the group consisting of X¹, X², X³, X⁴ and X⁵ may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted
10 cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

R² may be an optionally substituted alkyl or optionally substituted aryl.

X⁷ may be O or S.

A⁷ may be CH, CH₂ or N.

15  may be where the compound of Formula (IIIa) or (IIIb) is fused to the compound of Formula (I) of Formula (IV).

q may be 0 or 1.

t may be an integer selected from 1 to 4.

X⁸, X⁹, X¹¹ and X¹² may independently be absent or selected from the group consisting of a bond, H,
20 halogen, CN, R³, OR³ or SR³.

R³ may be selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl.

25 A⁸ may be selected from the group consisting of O, S, Se, Te, C and N.

A⁹, A¹⁰, A¹¹, A¹² and A¹³ may independently be C or N.

Any two substituents selected from the group consisting of X⁸, X⁹, X¹⁰, X¹¹ and X¹² may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted
30 cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

a may be any value from 0 to 1.

b may be an integer selected from 1 to 10,000.

y may be an integer selected from 0 to 5.

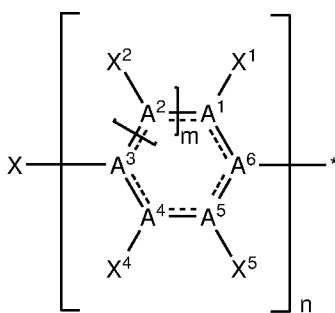
35 Optionally substituted alkyl may be an optionally substituted C₁-C₂₅ alkyl, optionally substituted alkenyl may be an optionally substituted C₂-C₂₅ alkenyl, optionally substituted alkynyl may be an optionally substituted C₂-C₂₅ alkynyl, optionally substituted cycloalkyl may be an optionally

- substituted C₃-C₁₂ cycloalkyl, optionally substituted heterocycloalkyl may be an optionally substituted C₃-C₁₂ heterocycloalkyl, optionally substituted cycloalkenyl may be an optionally substituted C₃-C₁₂ cycloalkenyl, optionally substituted heterocycloalkenyl may be an optionally substituted C₃-C₁₂ heterocycloalkenyl, optionally substituted aryl may be an optionally substituted C₃-C₁₈ aryl and
- 5 optionally substituted heteroaryl may be an optionally substituted C₃-C₁₈ heteroaryl.

Optionally substituted heterocycloalkyl and optionally substituted heteroaryl may independently be a 3- to 18-membered monocyclic, bicyclic, or polycyclic ring.

P¹

- P¹ may be selected from the group consisting of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted tellurophene, optionally substituted pyrrole, optionally substituted phenylene, optionally substituted aza-phenylene, optionally substituted arylene diimide, optionally substituted fluorene, optionally substituted cabazole, optionally substituted dibenzodilole, optionally substituted benzooxodiazole, optionally substituted benzotriazole, optionally substituted benzothidiazole and any combination thereof.
- 10
- 15 The P¹ may have the following Formula (IIa);



(IIa).

m may be 0.

A¹ may be N. A¹ may be S.

- 20 A³, A⁴, A⁵ and A⁶ may be C.

X¹ may be H. X¹ may be absent.

X⁴ and X⁵ may independently be selected from the group consisting of H, R¹ and OR¹. R¹ may be an optionally substituted alkyl. X⁴ and X⁵ may be H.

X may be Br.

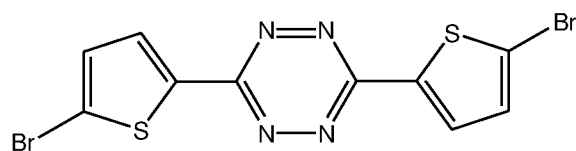
- 25 When m is 0, A¹ may be N, and X¹ may be H or optionally substituted alkyl.

When m is 0, A³, A⁴, A⁵ and A⁶ may be C, and X⁴ and X⁵ are independently selected from the group consisting of H, R¹ and OR¹, wherein R¹ is optionally substituted alkyl.

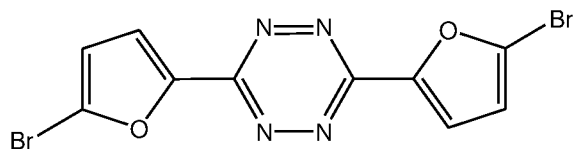
When m is 0, A¹ may be S; X¹ may be absent; A³, A⁴, A⁵ and A⁶ may be C, X⁴ and X⁵ may be H and X may be Br,

- 30 When m is 0, A¹ may be O; X¹ may be absent; A³, A⁴, A⁵ and A⁶ may be C, X⁴ and X⁵ may be H and X may be Br.

The compound may have the following formula (VIIIa) or (VIIIb):



(VIIIa)



(VIIIb).

5

m may be 1.

A¹, A², A³, A⁴, A⁵ and A⁶ may be C. A¹, A², A³ and A⁶ may be C. A³ and A⁶ may be C. A⁴ and A⁵ may be N. A⁴ and A⁵ may be C.

10 X¹, X², X⁴ and X⁶ may independently be absent or selected from the group consisting of H, halogen, R¹ and OR¹. X¹, X², X⁴ and X⁶ may independently be H or halogen. X⁴ and X⁵ may independently be H or F.

R¹ may be an optionally substituted alkyl.

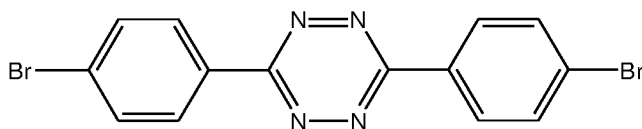
X¹ and X² may be taken together to form an optionally substituted 5-membered heteroaryl.

15 When m is 1, A³ and A⁶ may be C and X¹, X², X⁴ and X⁶ may be independently absent or selected from the group consisting of H, halogen, R¹ and OR¹, wherein R¹ is optionally substituted alkyl.

When m is 1, A¹, A², A³, A⁴, A⁵ and A⁶ may be C and X¹, X², X⁴ and X⁶ may independently be H or halogen.

When m is 1, A¹, A², A³, A⁴, A⁵ and A⁶ may be C and X¹, X², X⁴ and X⁶ may be H.

The compound may have the following Formula (VIIIc):

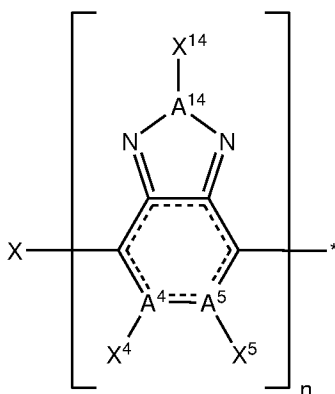


(VIIIc).

20

When m is 1, A¹, A², A³ and A⁶ may be C and X¹ and X² may be taken together to form an optionally substituted 5-membered heteroaryl.

P¹ may have the following formula (IX);



(IX)

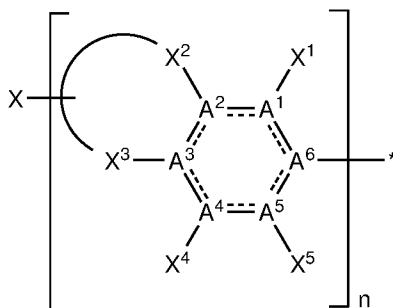
A¹⁴ may be selected from the group consisting of O, S, Se, Te and N.

5 X¹⁴ may be absent or optionally substituted alkyl.

When P¹ has the formula (IX), A⁴ and A⁵ may be N.

When P¹ has the formula (IX), A⁴ and A⁵ may be C; and X⁴ and X⁵ may independently be H or F.

P¹ may have the following Formula (IIb);



(IIb).

A¹, A², A³, A⁴, A⁵ and A⁶ may be C.

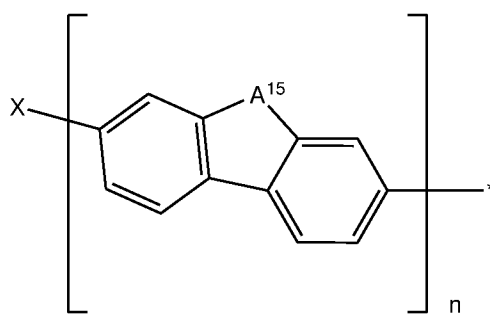
X¹, X⁴ and X⁵ may be H.

X² and X³ may be taken together to form an optionally substituted 5-membered heterocycloalkyl. X² and X³ may be taken together to form an optionally substituted 6-membered heterocycloalkyl. X³ and

15 X⁴ may be taken together to form an optionally substituted a 6-membered aryl. X⁴ and X⁵ may be taken together to form an optionally substituted 6-membered heterocycloalkyl.

The optionally substituted 5-membered heterocycloalkyl may be further fused with an optionally substituted 6-membered aryl.

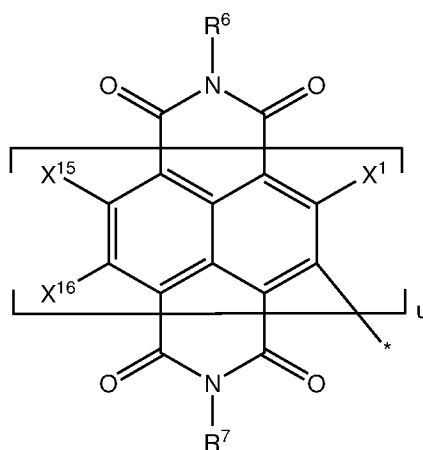
P¹ may have the following formula (X);



(X)

A¹⁵ may be selected from the group consisting of NH, C(R⁴)₂, and Si(R⁴)₂. R⁴ may be an optionally substituted alkyl.

P¹ may have the following Formula (XI);



(XI)

X¹, X¹⁵ and X¹⁶ may independently be selected from the group consisting of H, halogen and CN.

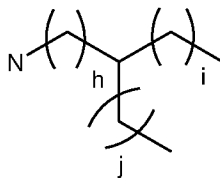
R⁶ and R⁷ may independently be selected from the group consisting of H, R⁸ and OR⁸, wherein R⁸ is optionally substituted alkyl.

u may be 1 or 2.

P²

P² may be selected from the group consisting of optionally substituted imide and optionally substituted phthalamide.

R² may be an optionally substituted alkyl. The optionally substituted alkyl may be an optionally substituted linear alkyl or an optionally substituted branched alkyl. The optionally substituted linear alkyl may be an optionally substituted C₁ to C₂₅ linear alkyl. The optionally substituted branched alkyl may be an optionally substituted C₁ to C₂₅ branched alkyl. The optionally substituted branched alkyl may have the following formula (XII).



(XII)

N of Formula (XII) may be where the R^2 group is connected to the rest of the compound in Formulae (IVa), (IVb), (IVc), (IVd), (VIIa) or (VIIb).

- 5 h may be 0 or 1. i and j may independently be integers selected from 1 to 13. h may be 1. i may be 7. j may be 9.

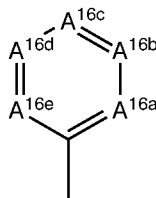
The optionally substituted alkyl may be 2-ethylheptyl, 2-heptylhexadecyl, 2-heptylpentadecyl, 2-heptyltetradecyl, 2-heptyltridecyl, 2-heptyldodecyl, 2-heptylundecyl, 2-heptyldecyl, 2-heptylnonyl, 2-heptyloctyl, 2-heptylheptyl, 2-octylhexadecyl, 2-octylpentadecyl, 2-octyltetradecyl, 2-octyltridecyl, 2-octyldodecyl, 2-octylundecyl, 2-octyldecyl, 2-octylnonyl, 2-octyloctyl, 2-nonyltetradecyl, 2-nonyltridecyl, 2-nonyldodecyl, 2-nonylundecyl, 2-nonyldecyl or 2-nonylnonyl.

10

The optionally substituted may be any linear or branched alkyl chain that may confer improved solubility and processability of the final product.

X^7 may be O.

- 15 R^2 may be an optionally substituted aryl having the following Formula (XIII);

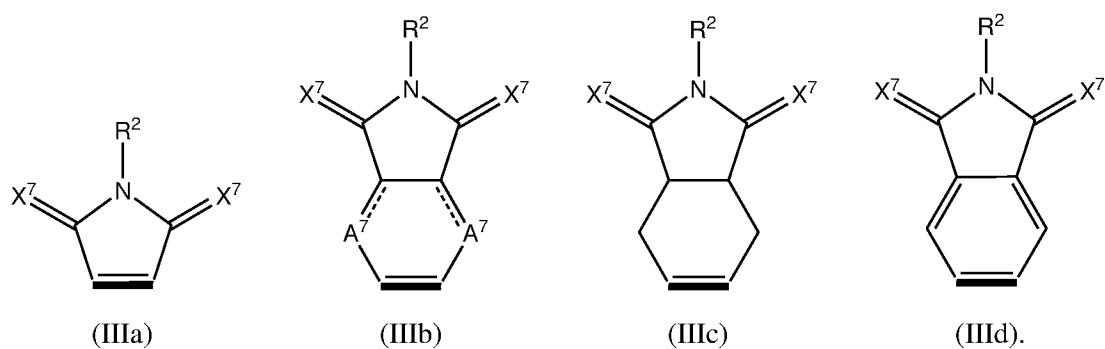


(XIII)

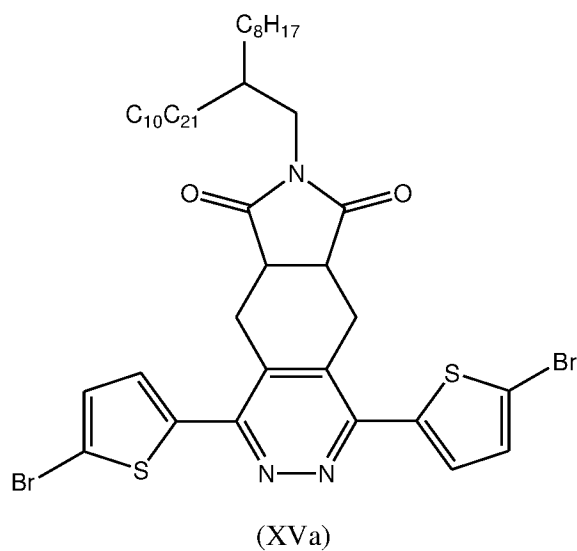
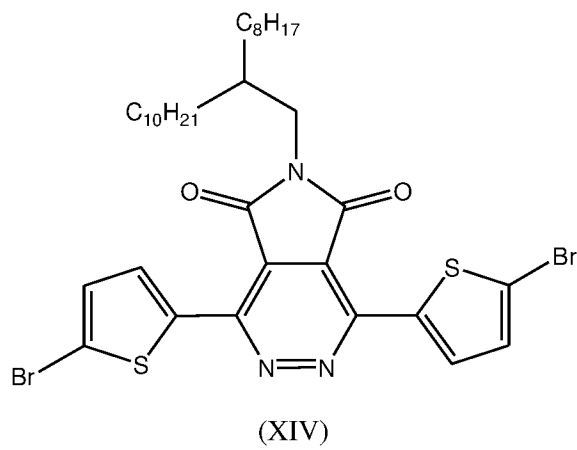
- 20 A^{16a} , A^{16b} , A^{16c} , A^{16d} and A^{16e} may independently be selected from the group consisting of N, CH and CR^9 , wherein R^9 is an optionally substituted alkyl. A^{16a} may be N and A^{16b} , A^{16c} , A^{16d} and A^{16e} may be CH. A^{16b} may be N and A^{16a} , A^{16c} , A^{16d} , A^{16e} may be CH. A^{16c} may be N and A^{16a} , A^{16b} , A^{16d} and A^{16e} may be CH. A^{16b} and A^{16d} may be N and A^{16a} , A^{16c} , A^{16d} and A^{16e} may be CH. A^{16a} , A^{16c} , A^{16e} may be N and A^{16b} and A^{16d} may be CH.

A^7 may be CH, A^7 may be CH_2 .

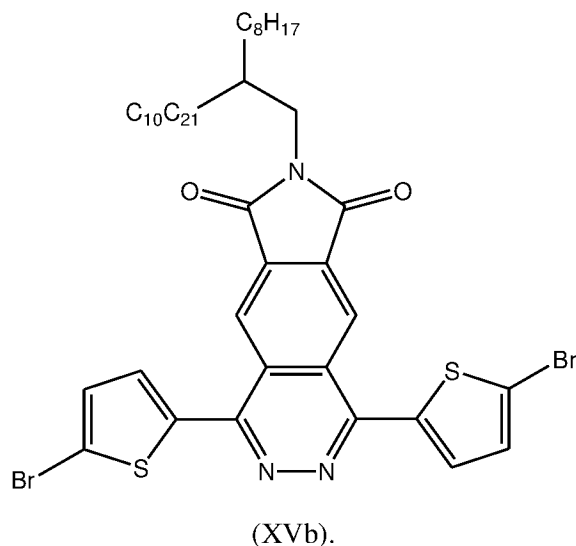
P² may have the following formula (IIIa), (IIIb), (IIIc), or (IIIId):



The compound may have the following formula (XIV), (XVa) or (XVb):



33



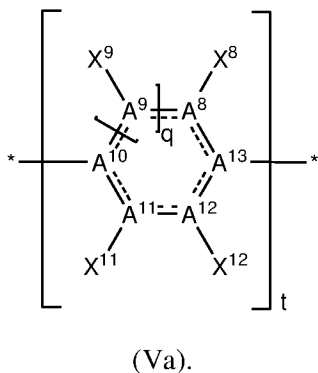
The compound of Formula (I) may be 6-alkyl-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (PPD). PPD may lower the frontier orbitals of the polymers to make the polymer more stable under ambient conditions.

P^3

P^3 may be a moiety that performs as a good electron donor in electrochromic materials. The chemical and physical nature of the P^3 group may enhance the solubility and processability of the final polymer materials as well as the performance of the polymer films under voltage bias.

P^3 may be selected from the group consisting of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted pyrrole, optionally substituted phenyl, optionally substituted fluorenes, optionally substituted carbazoles, optionally substituted fused furans and optionally substituted fused thiophenes.

P^3 may have the following formula (Va);



q may be 0.

A^8 may be N. A^8 may be S. A^{10} , A^{11} , A^{12} and A^{13} may be C.

X^8 may be H or an optionally substituted alkyl. X^8 may be absent. X^{11} and X^{12} may independently be selected from the group consisting of H, R^3 and OR^3 . R^3 may be optionally substituted alkyl.

X^{11} and X^{12} may be taken together to form an optionally substituted 7-membered heterocycloalkyl.

When q is 0, A^8 may be N, A^{10} , A^{11} , A^{12} and A^{13} may be C, X^8 may be H and X^{11} and X^{12} may independently be selected from the group consisting of H, R^3 and OR^3 , wherein R^3 is optionally substituted alkyl.

When q is 0, A^8 may be S; X^8 may be absent; A^{10} , A^{11} , A^{12} and A^{13} may be C and X may be Br.

- 5 When q is 0, A^8 may be S; X^8 may be absent; A^{10} , A^{11} , A^{12} and A^{13} may be C, and X^{11} and X^{12} may be taken together to form an optionally substituted 7-membered heterocycloalkyl. The optionally substituted 7-membered heterocycloalkyl may be substituted with two alkoxy groups. The alkoxy group may be $OC_{12}H_{25}$.

q may be 1.

- 10 A^8 , A^9 , A^{10} , A^{11} , A^{12} and A^{13} may be C. A^{10} and A^{13} may be C.

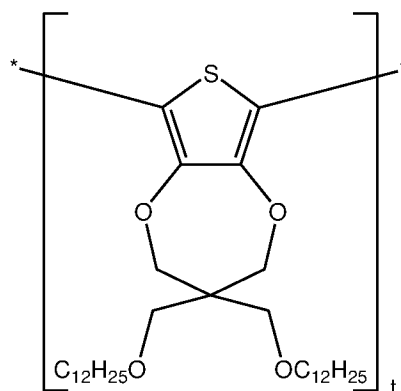
X^8 , X^9 , X^{11} and X^{12} may independently be selected from the group consisting of H, halogen, R^3 and OR^3 . R^3 may be an optionally substituted alkyl. X^8 , X^9 , X^{11} and X^{12} may be independently selected from the group consisting of H, halogen, OR^{10} and SR^{10} . R^{10} may be an optionally substituted alkyl.

- 15 When q is 1, A^{10} and A^{13} may be C; X^8 , X^9 , X^{11} and X^{12} may independently be selected from the group consisting of H, halogen, R^3 and OR^3 , wherein R^3 may be optionally substituted alkyl.

When q is 1, A^8 , A^9 , A^{10} , A^{11} , A^{12} and A^{13} may be C and X^8 , X^9 , X^{11} and X^{12} may independently be selected from the group consisting of H, halogen, OR^{10} and SR^{10} , wherein R^{10} may be an optionally substituted alkyl.

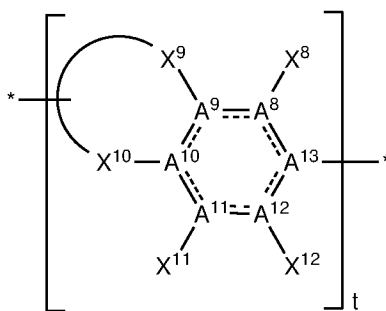
- 20 P^3 may be a 3,4-dialkoxythiophene.

P^3 may have the following Formula (XVI);



(XVI).

P³ may have the following formula (Vb);



(Vb).

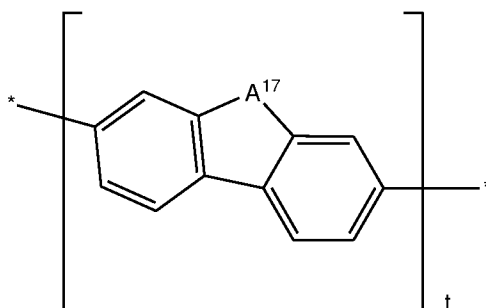
A⁸, A⁹, A¹⁰, A¹¹, A¹² and A¹³ may be C.

5 X⁸, X¹¹ and X¹² may be H.

X⁹ and X¹⁰ may be taken together to form an optionally substituted 5-membered heterocycloalkyl.

The optionally substituted 5-membered heterocycloalkyl may be further fused with an optionally substituted 6-membered aryl.

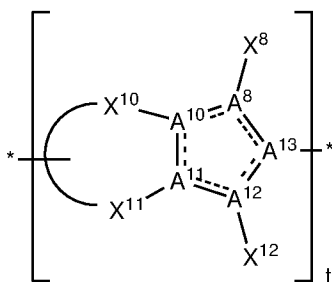
P³ may have the following formula (XVII);



(XVII)

A¹⁷ may be selected from the group consisting of NH, C(R¹¹)₂, and Si(R¹¹)₂. R¹¹ may be optionally substituted alkyl. R¹¹ may be C₈H₁₇.

P³ may have the following Formula (Vc);

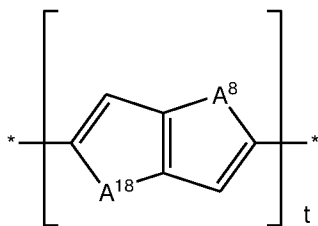


(Vc).

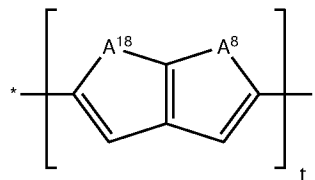
A¹⁰, A¹¹, A¹² and A¹³ may be C. X⁸ and X¹² may be H.

X^{10} and X^{11} may be taken together to form an optionally substituted 5-membered heteroaryl. X^{10} and X^{11} may be taken together to form an optionally substituted 6-membered aryl. The optionally substituted 6-membered aryl may be further fused with an optionally substituted 5-membered heteroaryl.

5 P^3 may have the following Formula (XVIIIa) or (XVIIIb);



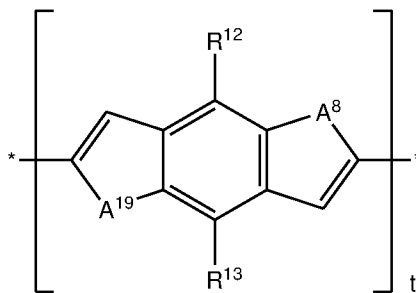
(XVIIIa)



(XVIIIb)

A^8 and A^{18} may be independently selected from the group consisting of O, S and Se.

P^3 may have the following Formula (XIX);



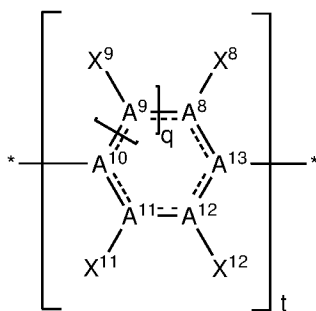
(XIX)

A^8 and A^{19} may independently be selected from the group consisting of O, Se and S. R^{12} and R^{13} may independently be selected from the group consisting of R^{14} , OR^{14} and SR^{14} . R^{14} may be optionally substituted alkyl or optionally substituted aryl. R^{14} may be an optionally substituted alkyl. R^{14} may be C_8H_{17} . R^{14} may be a 2-ethylheptyl group.

P^4

P^4 may be absent, or selected from the group consisting of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted pyrrole, optionally substituted phenyl, optionally substituted fluorenes, optionally substituted carbazoles, optionally substituted fused furans and optionally substituted fused thiophenes.

P⁴ may have the following formula (Va);



(Va).

q may be 0.

- 5 A⁸ may be N. A⁸ may be S. A¹⁰, A¹¹, A¹² and A¹³ may be C.

X⁸ may be H or an optionally substituted alkyl. X⁸ may be absent. X¹¹ and X¹² may independently be selected from the group consisting of H, R³ and OR³. R³ may be optionally substituted alkyl.

X¹¹ and X¹² may be taken together to form an optionally substituted 7-membered heterocycloalkyl.

- 10 When q is 0, A⁸ may be N, A¹⁰, A¹¹, A¹² and A¹³ may be C, X⁸ may be H and X¹¹ and X¹² may independently be selected from the group consisting of H, R³ and OR³, wherein R³ is optionally substituted alkyl.

When q is 0, A⁸ may be S; X⁸ may be absent and A¹⁰, A¹¹, A¹² and A¹³ may be C.

- 15 When q is 0, A⁸ may be S; X⁸ may be absent; A¹⁰, A¹¹, A¹² and A¹³ may be C and X¹¹ and X¹² may be taken together to form an optionally substituted 7-membered heterocycloalkyl. The optionally substituted 7-membered heterocycloalkyl may be substituted with two alkoxy groups. The alkoxy groups may be OC₁₂H₂₅.

q may be 1.

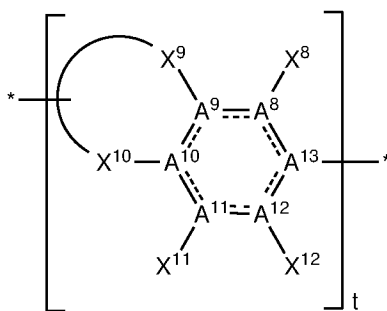
A⁸, A⁹, A¹⁰, A¹¹, A¹² and A¹³ may be C. A¹⁰ and A¹³ may be C.

- 20 X⁸, X⁹, X¹¹ and X¹² may independently be selected from the group consisting of H, halogen, R³ and OR³. R³ may be an optionally substituted alkyl. X⁸, X⁹, X¹¹ and X¹² may be independently selected from the group consisting of H, halogen, OR¹⁰ and SR¹⁰. R¹⁰ may be an optionally substituted alkyl.

When q is 1, A¹⁰ and A¹³ may be C; X⁸, X⁹, X¹¹ and X¹² may independently be selected from the group consisting of H, halogen, R³ and OR³, wherein R³ may be optionally substituted alkyl.

- 25 When q is 1, A⁸, A⁹, A¹⁰, A¹¹, A¹² and A¹³ may be C and X⁸, X⁹, X¹¹ and X¹² may independently be selected from the group consisting of H, halogen, OR¹⁰ and SR¹⁰, wherein R¹⁰ may be an optionally substituted alkyl.

P⁴ may have the following formula (Vb);



(Vb).

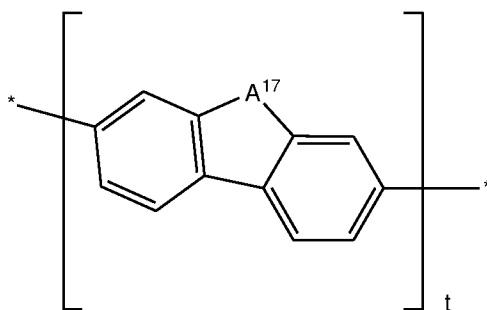
A⁸, A⁹, A¹⁰, A¹¹, A¹² and A¹³ may be C.

5 X⁸, X¹¹ and X¹² may be H.

X⁹ and X¹⁰ may be taken together to form an optionally substituted 5-membered heterocycloalkyl.

The optionally substituted 5-membered heterocycloalkyl may be further fused with an optionally substituted 6-membered aryl.

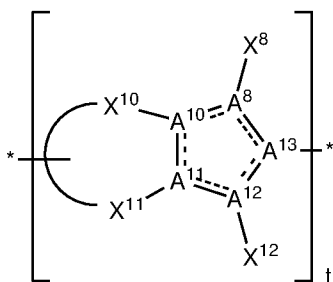
P⁴ may have the following formula (XVII);



(XVII)

A¹⁷ may be selected from the group consisting of NH, CHR¹¹, C(R¹¹)₂, SiHR¹¹ and Si(R¹¹)₂. R¹¹ may be optionally substituted alkyl. R¹¹ may be C₈H₁₇ or C₁₂H₂₅.

P⁴ may have the following Formula (Vc);

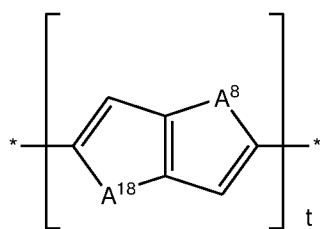


(Vc).

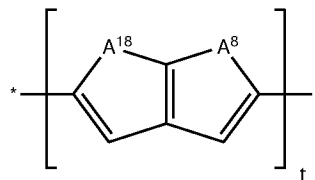
A¹⁰, A¹¹, A¹² and A¹³ may be C. X⁸ and X¹² may be H.

X^{10} and X^{11} may be taken together to form an optionally substituted 5-membered heteroaryl. X^{10} and X^{11} may be taken together to form an optionally substituted 6-membered aryl. The optionally substituted 6-membered aryl may be further fused with an optionally substituted 5-membered heteroaryl.

5 P^4 may have the following Formula (XVIIIa) or (XVIIIb);



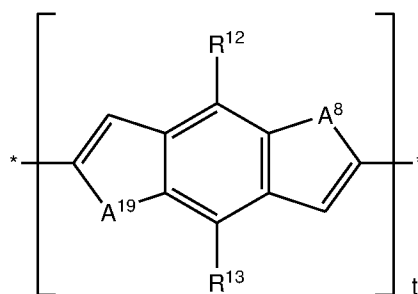
(XVIIIa)



(XVIIIb)

A^8 and A^{18} may be independently selected from the group consisting of O, S and Se.

P^4 may have the following Formula (XIX);

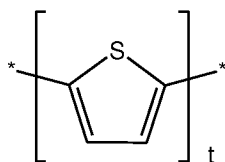


(XIX)

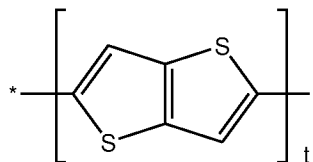
A^8 and A^{19} may independently be selected from the group consisting of O, Se and Se. R^{12} and R^{13} may independently be selected from the group consisting of R^{14} , OR^{14} and SR^{14} . R^{14} may be optionally substituted alkyl or optionally substituted aryl. R^{14} may be an optionally substituted alkyl.

15 P^4 may be an optionally substituted thiophene or an optionally substituted fused thiophene.

P^4 may have the following Formula (XXXIa) or (XXXIb):



(XXXIa)



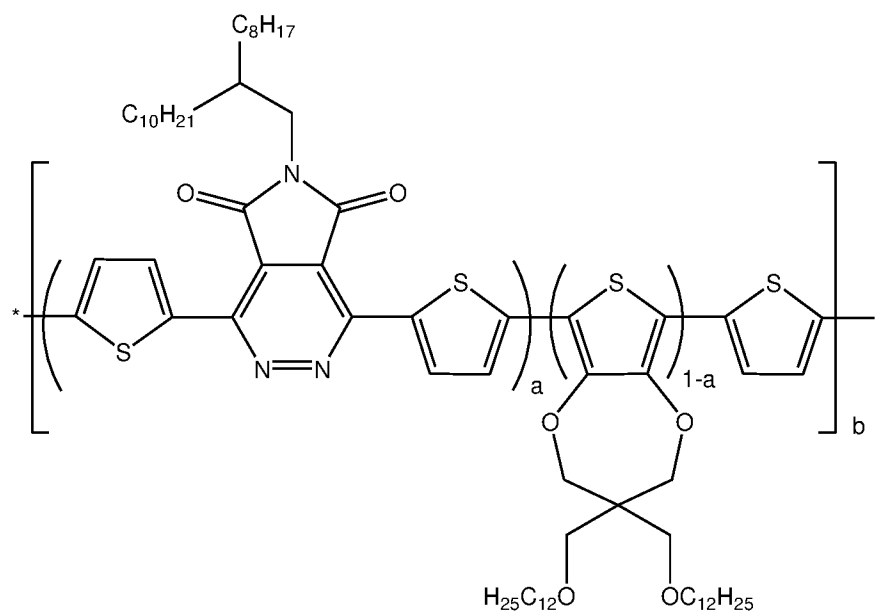
(XXXIb)

a may be 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2 or 0.1. a may be 0.5, 0.3 or 0.1.

20 b may be an integer selected from 1 to 50, 1 to 10, 1 to 20, 1 to 30, 1 to 40, 10 to 20, 10 to 30, 10 to 40, 10 to 50, 20 to 30, 20 to 40, 20 to 50, 30 to 40, 30 to 50 or 40 to 50.

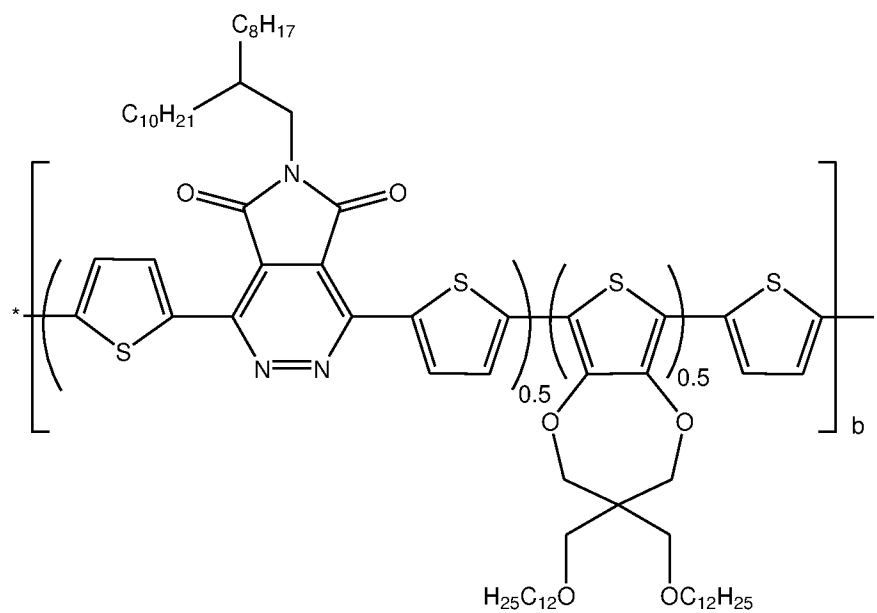
y may be 1. y may be 2.

The compound may have the following formula (XX):

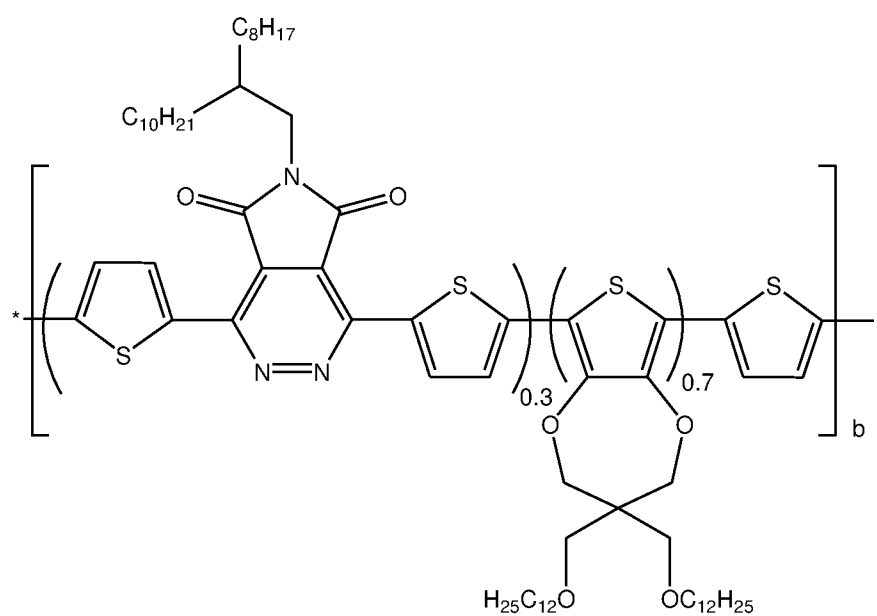


(XX).

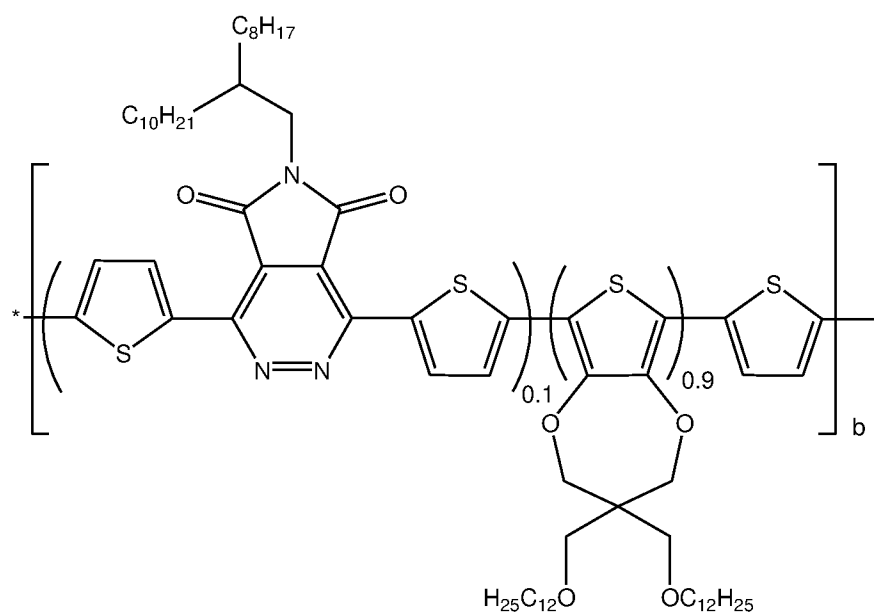
The compound may have the following formula (XXa), (XXb) or (XXc):



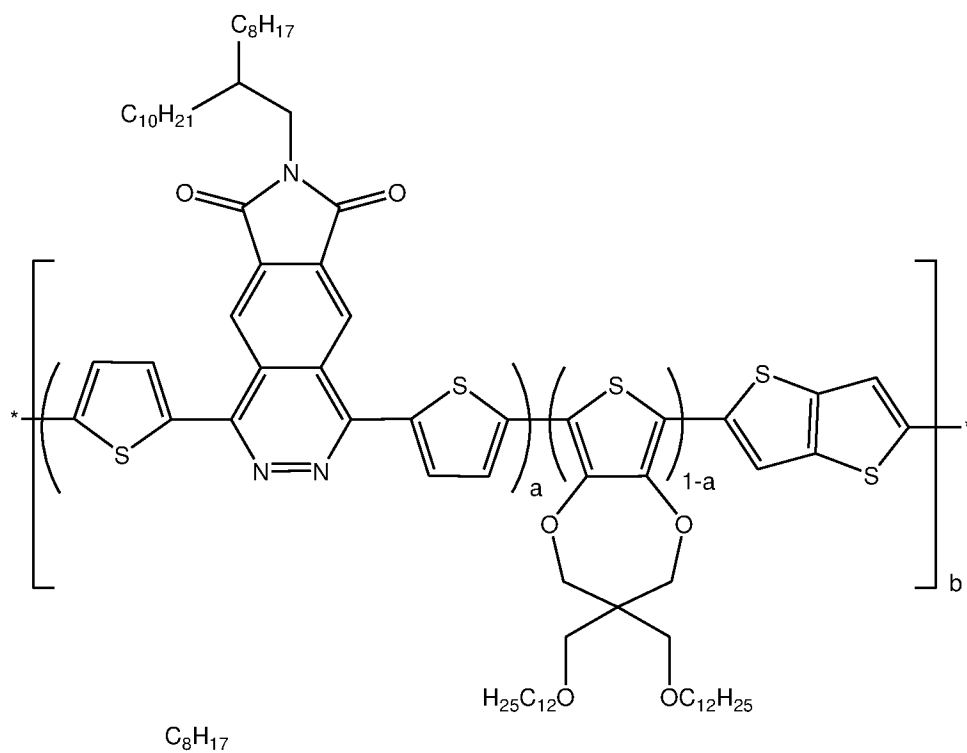
(XXa)



(XXb)

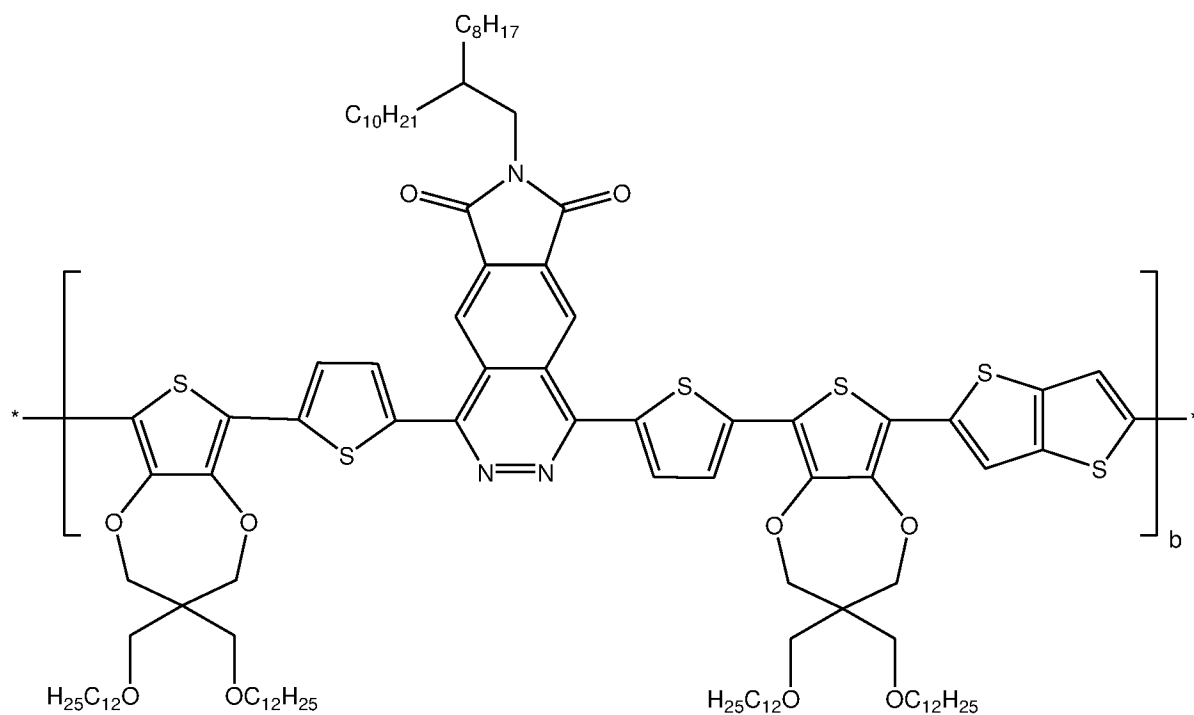


(XXc)



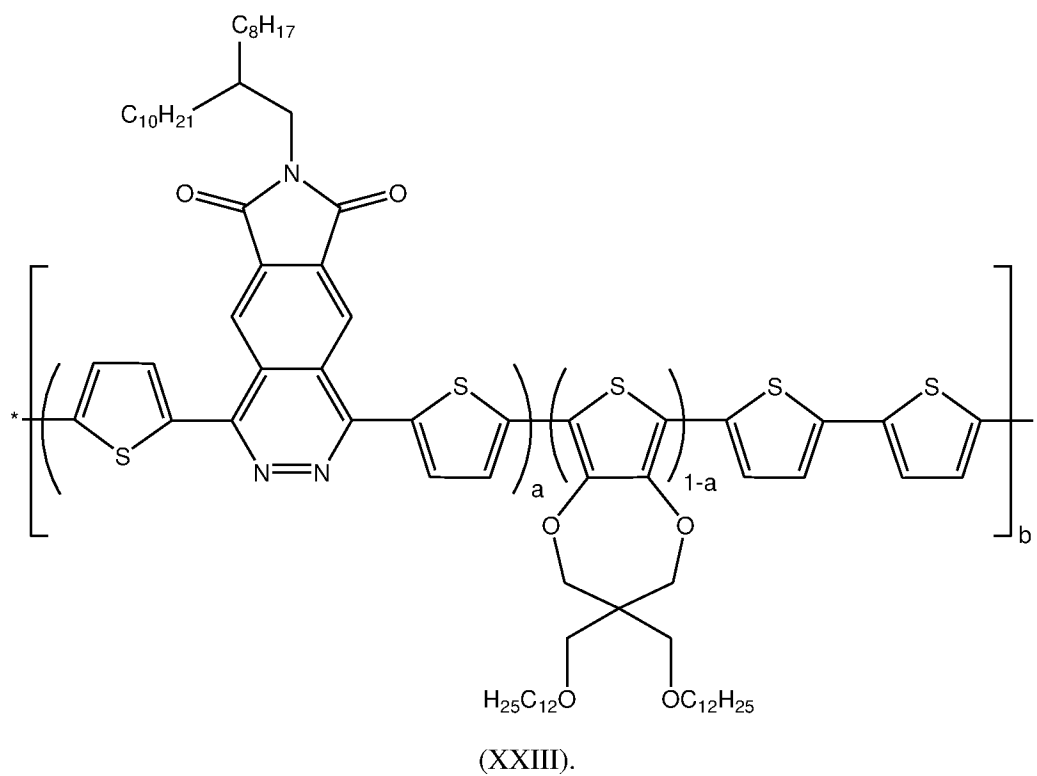
(XXII).

The compound may have the following formula (XXIIa):

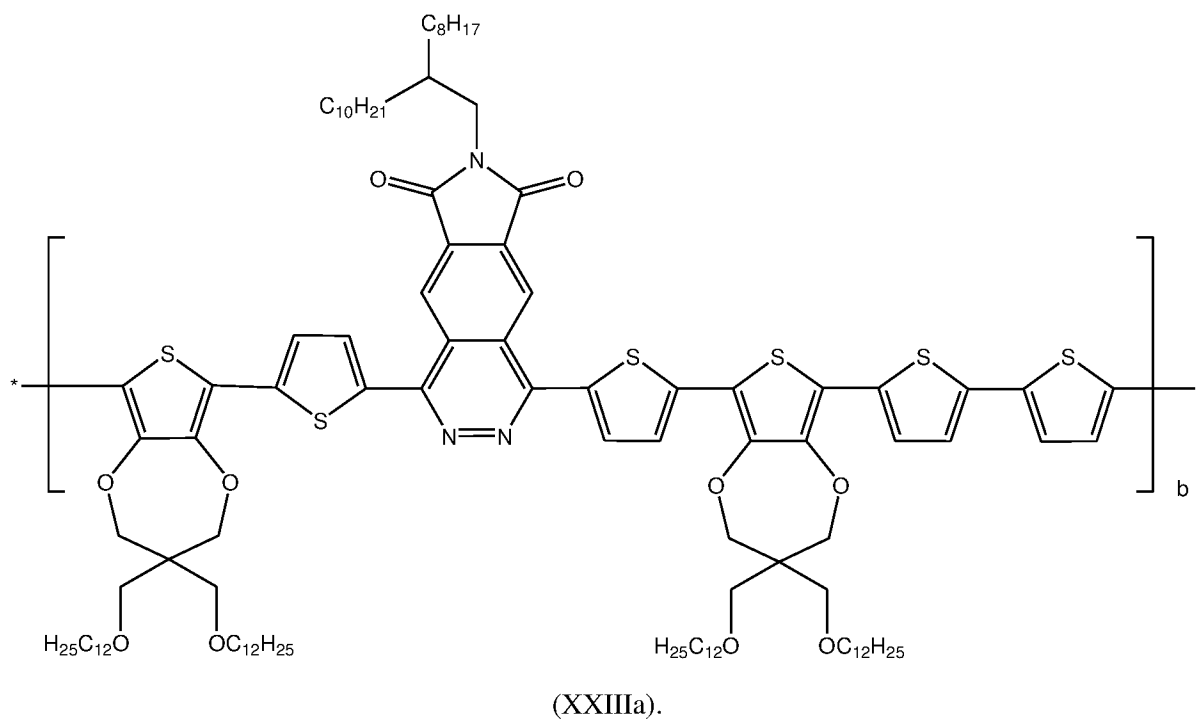


(XXIIa).

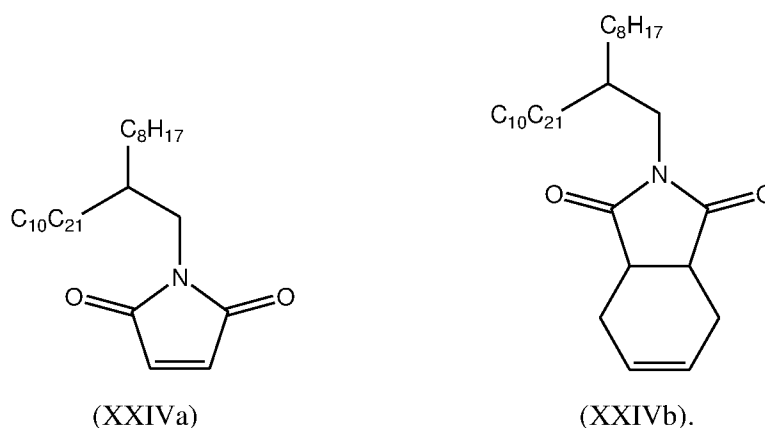
The compound may have the following formula (XXIII):



5 The compound may have the following formula (XXIIIa):



The compound may have the following Formula (XXIVa) or (XXIVb):



- 5 A method for synthesizing the compound of Formula (VI) as defined above may comprise the steps of providing a hydrazine and contacting the hydrazine with a functionalized cyclic group, wherein the cyclic group of the functionalized cyclic group is selected from the group comprising of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted tellurophene, optionally substituted pyrrole, optionally substituted phenylene, optionally substituted aza-phenylene, optionally substituted arylene diimide, optionally substituted fluorene, optionally substituted cabazole, optionally substituted dibenzodilole, optionally substituted benzoxodiazole, optionally substituted benzotriazole, optionally substituted benzothidiazole and any combination thereof.

The functionalized cyclic group may be functionalized with at least one nitrile (CN) group.

The functionalized cyclic group may be 2-cyanothiophene.

- 15 A method for synthesizing the compound of Formula (I) as defined above may comprise the steps of:
 providing the compound of Formula (IV) as defined above; and
 contacting the compound of Formula (IV) as defined above with the compound (VIIa) or (VIIb) as defined above under reaction conditions to form the compound of Formula (III) as defined above. The method for synthesizing the compound of Formula (I) as defined above may comprise an inverse-electron demanding Diels-Alder reaction. An inverse-electron demanding Diels-Alder reaction is an organic chemical reaction in which two new chemical bonds and a six-membered ring are formed. It is related to the Diels-Alder reaction, whereby an organic chemical reaction between a conjugated diene and a substituted alkene, commonly termed the dienophile, forms a substituted cyclohexene system. However, unlike the Diels-Alder reaction, the inverse electron demand Diels-Alder reaction is a cycloaddition between an electron-rich dienophile and an electron-poor diene. During an inverse-electron demand Diels-Alder reaction, three pi-bonds are broken and two sigma bonds and one new pi-bond are formed. In the present disclosure, the electronic nature of the reaction partners for an inverse Diels-Alder reaction is inversed again. The tetrazine, as the diene being used herein, may have electron-donating substituents, such as thiophenes, and is therefore considered electron-rich. The dienophile may be an intrinsically electron-poor moiety, such as an imide. This may result in synthetic challenges, which are solved by an inventive choice of solvents and reaction conditions.

The compounds of the formula (XXIVa) and (XXIVb) may both comprise electron withdrawing imides. The compounds of formula (XXIVa) and (XXIVb) may be reacted independently with the compound of Formula (I) to form the compound of Formula (III).

5 The compound of Formula (VIIa) or (VIIb) may be contacted with the compound of Formula (VI) to form P^2 in the compound of Formula (I). When the compound of Formula (VIIa) is contacted with the compound of Formula (VI), P^2 of the compound of Formula (I) may have the Formula (IIIa). When the compound of Formula (VIIb) is contacted with the compound of Formula (VI), P^2 of the compound of Formula (I) may have the Formula (IIIb).

10 The method as defined above may be performed under reaction conditions. Reaction conditions may refer to the solvent, reaction temperature and duration of reaction. The choice of solvent, temperature and duration for the reaction for forming the compound of Formula (I) may be very important.

15 The solvent may be selected from the group consisting of chloroform, dichloromethane, tetrachloromethane, tetrahydrofuran, dioxane, diphenyl ether, toluene, chlorobenzene, dichlorobenzene, xylene and any mixture thereof. The solvent may not contain any reactivity towards the reaction mixture.

20 The reaction temperature may be in the range of about 40 °C to about 200 °C, about 40 °C to about 60 °C, about 40 °C to about 80 °C, about 40 °C to about 100 °C, about 40 °C to about 120 °C, about 40 °C to about 140 °C, about 40 °C to about 160 °C, about 40 °C to about 180 °C, about 60 °C to about 80 °C, about 60 °C to about 100 °C, about 60 °C to about 120 °C, about 60 °C to about 140 °C, about 60 °C to about 160 °C, about 60 °C to about 180 °C, about 60 °C to about 200 °C, about 80 °C to about 100 °C, about 80 °C to about 120 °C, about 80 °C to about 140 °C, about 80 °C to about 160 °C, about 80 °C to about 180 °C, about 80 °C to about 200 °C, about 100 °C to about 120 °C, about 100 °C to about 140 °C, about 100 °C to about 160 °C, about 100 °C to about 180 °C, about 100 °C to about 200 °C, about 120 °C to about 140 °C, about 120 °C to about 160 °C, about 120 °C to about 180 °C, about 120 °C to about 200 °C, about 140 °C to about 160 °C, about 140 °C to about 180 °C, about 140 °C to about 200 °C, about 160 °C to about 180 °C, about 160 °C to about 200 °C or about 180 °C to about 200 °C. The boiling point of the solvent may be sufficiently high to allow the reaction to proceed.

30 The duration of reaction may be in the range of about 4 hours to about 24 hours, about 4 hours to about 6 hours, about 4 hours to about 8 hours, about 4 hours to about 10 hours, about 4 hours to about 12 hours, about 4 hours to about 18 hours, about 4 hours to about 24 hours, about 6 hours to about 8 hours, about 6 hours to about 10 hours, about 6 hours to about 12 hours, about 6 hours to about 18 hours, about 6 hours to about 24 hours, about 8 hours to about 10 hours, about 8 hours to about 12 hours, about 8 hours to about 18 hours, about 8 hours to about 24 hours, about 10 hours to about 12 hours, about 10 hours to about 18 hours, about 10 hours to about 24 hours, about 12 hours to about 18 hours, about 12 hours to about 24 hours or about 18 hours to about 24 hours.

The reaction may proceed efficiently when diphenyl ether is used as the solvent and the reaction temperature is about 160 °C and the reaction duration is about 12 hours. If a solvent with a lower boiling point is used, for example, such that the reaction temperature cannot reach a sufficiently high temperature, the reaction may not proceed efficiently or at all even after 12 hours.

40 The method may further comprise the step of reacting the compound of Formula (III) as defined above with N-bromosuccinimide. The method may further comprise the step of reacting the

compound of Formula (I) as defined above with N-bromosuccinimide and a peroxide, followed by a base when P² of Formula (I) has the Formula (IIIc). When the P² of the compound of Formula (I) has the Formula (IIIc), and this is reacted with N-bromosuccinimide and a peroxide, followed by a base, the resulting compound is the compound of Formula (I) where P² has the Formula (IIIId). The method may further comprise the step of reacting the compound of Formula (XVa) as defined above with N-bromosuccinimide and a peroxide, followed by a base, resulting in the formation of the compound of Formula (XVb).

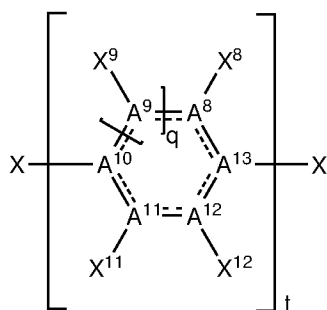
The step of reacting the compound of Formula (I) as defined above with N-bromosuccinimide may be performed in a solvent selected from the group consisting of chloroform, trichloromethane, benzene and any mixture thereof.

The peroxide may be hydrogen peroxide or benzoyl peroxide. The peroxide may be benzoyl peroxide. The base may be triethylamine.

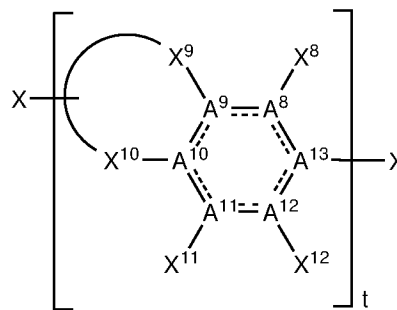
A method for synthesizing the compound of Formula (IV) as defined above may comprise the steps of:

providing the compound of Formula (I) as defined above; and

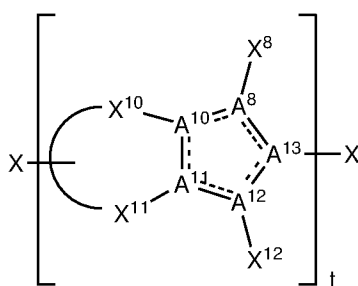
contacting the compound of Formula (I) as defined above with a compound having the following Formula (XVIIa), (XVIIb) or (XVIIc):



(XVIIa)



(XVIIb)

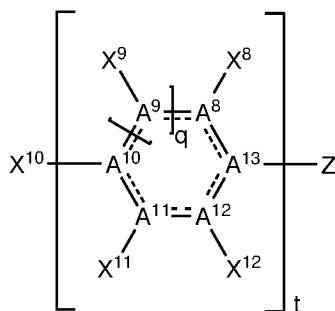


(XVIIc)

and a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group may be selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl; in the presence of a metal-containing catalyst.

A method for synthesizing the compound of Formula (IV) as defined above, comprising the steps of:

- 1) providing the compound of Formula (I) as defined above; and
- 2) contacting the compound of Formula (I) as defined above with a compound having the following Formula (XXVI) in the presence of a metal-containing catalyst to form a monomer precursor:



(XXVI)

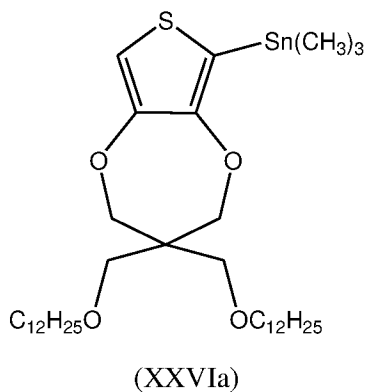
where Z may be a functional group containing zinc, tin or boron. Z may be $\text{Sn}(\text{CH}_3)_3$ or $\text{Sn}(\text{C}_4\text{H}_9)_3$;

- 3) reacting the monomer precursor of step (2) with N-bromosuccinimide to form a reactive monomer; and

- 4) reacting the reactive monomer of step (2) with a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group is selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl; in the presence of a metal-containing catalyst.

When q is 0, A^8 may be S; X^8 may be absent; A^{10} , A^{11} , A^{12} and A^{13} may be C, Z may be $\text{Sn}(\text{CH}_3)_3$ X^{10} may be H and X^{11} and X^{12} may be taken together to form an optionally substituted 7-membered heterocycloalkyl. The optionally substituted 7-membered heterocycloalkyl may be substituted with two alkoxy groups. The alkoxy groups may be $\text{OC}_{12}\text{H}_{25}$.

The compound of Formula (XXVI) may have the following formula (XXVIa):

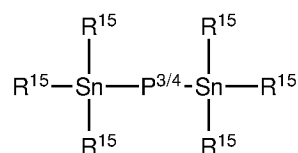


(XXVIa)

The metal in the metal-containing catalyst may be selected from the group consisting of palladium, nickel and copper. The metal-containing catalyst may be $\text{Pd}(\text{PPh}_3)_4$.

The cross-coupling reagent may comprise tin. The cross-coupling reagent may comprise boron.

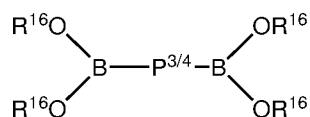
The cross-coupling reagent comprising tin may have the following formula (XXVII):



(XXVII)

wherein R^{15} may be an optionally substituted alkyl.

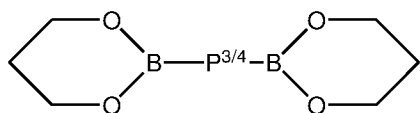
- 5 The cross-coupling reagent comprising boron may have the following formula (XXVIIIa);



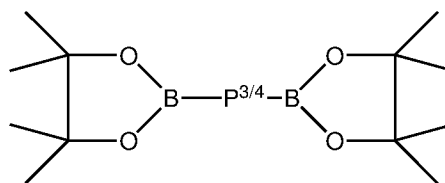
(XXVIIIa)

wherein R^{16} may be H or optionally substituted alkyl.

The cross-coupling reagent comprising boron may have the following formula (XXVIIIb) or (XXVIIIc):



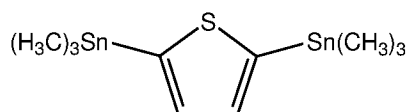
(XXVIIIb)



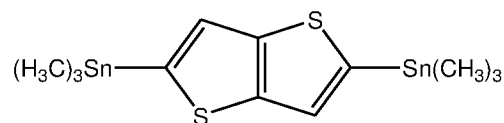
(XXVIIIc).

$\text{P}^{3/4}$ may refer to P^3 or P^4 .

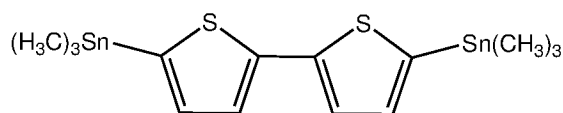
The cross-coupling reagent may have the following Formula (XXIXa), (XXIXb) or (XXIXc):



(XXIXa)

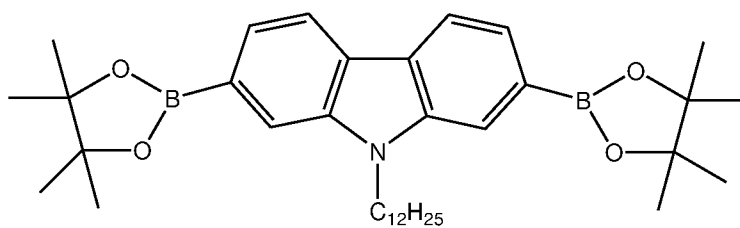


(XXIXb)



(XXIXc)

The cross-coupling reagent may have the following Formula (XXX):



(XXX).

Use of the compound as defined above may be in the manufacture of semiconductor devices.

- 5 A semiconductor device may comprise the compound of Formula (IV) as defined above.

Examples

Non-limiting examples of the disclosure and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

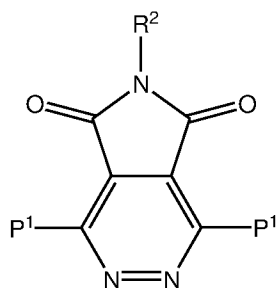
- 5 The synthetic steps are disclosed in a general manner in the following synthetic methods. Variations of these general methods in order to produce the polymers according to the present disclosure are within the ability of the person skilled in the art. Where representative procedures are given, these can be adjusted by the person skilled in the art to other derivatives, if needed.

10 EXAMPLE 1

Synthesized Monomers

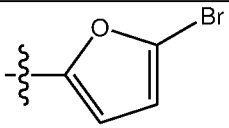
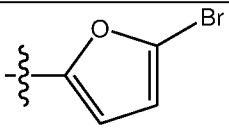
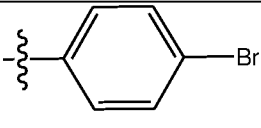
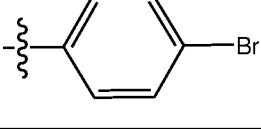
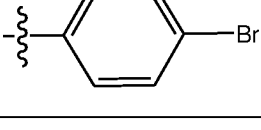
Pyridazines

Pyridazines synthesized having the following structure are shown in Table 1:



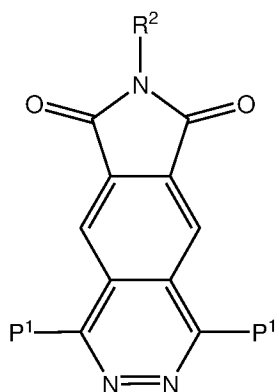
15 **Table 1: Pyradazine monomers**

Monomer name	P ¹	R ²
Monomer 1		hexyl
Monomer 2		dodecyl
Monomer 3		2-octyldodecyl
Monomer 4		hexyl

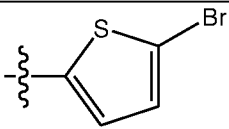
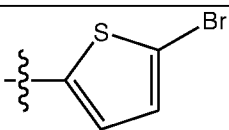
Monomer 5		dodecyl
Monomer 6		2-octyldodecyl
Monomer 7		hexyl
Monomer 8		dodecyl
Monomer 9		2-octyldodecyl

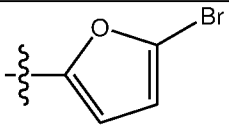
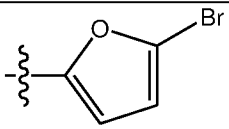
Phthalazines

Phthalazines synthesized having the following structure are shown in Table 2:



5 **Tabel 2: Phthalazine monomers**

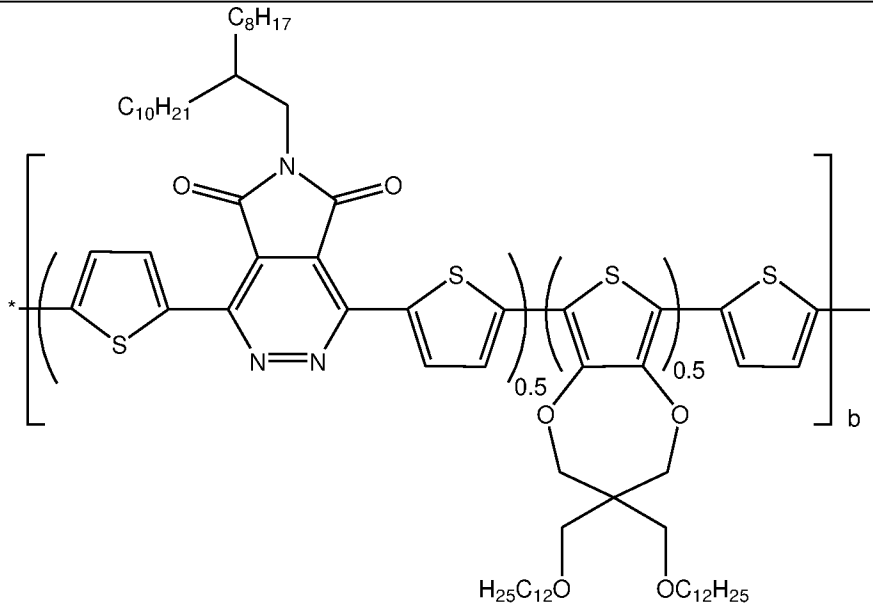
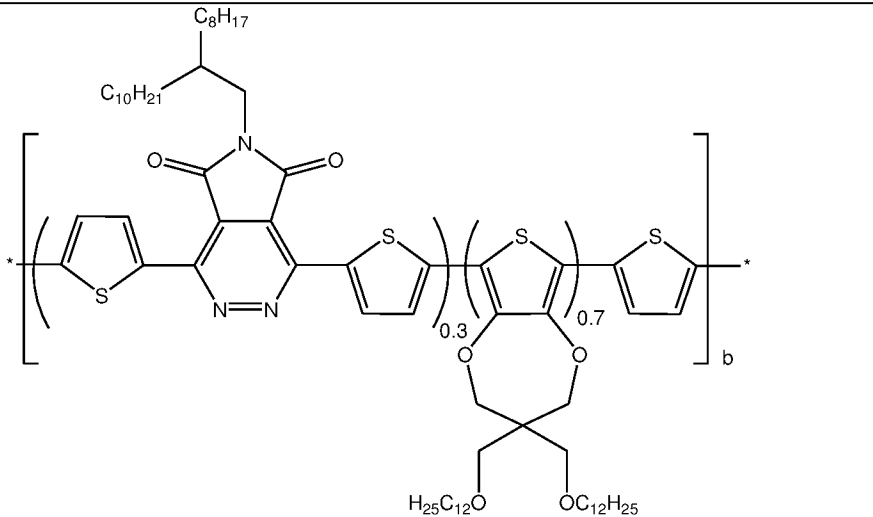
Monomer name	P¹	R²
Monomer 10		butyl
Monomer 11		2-octyldodecyl

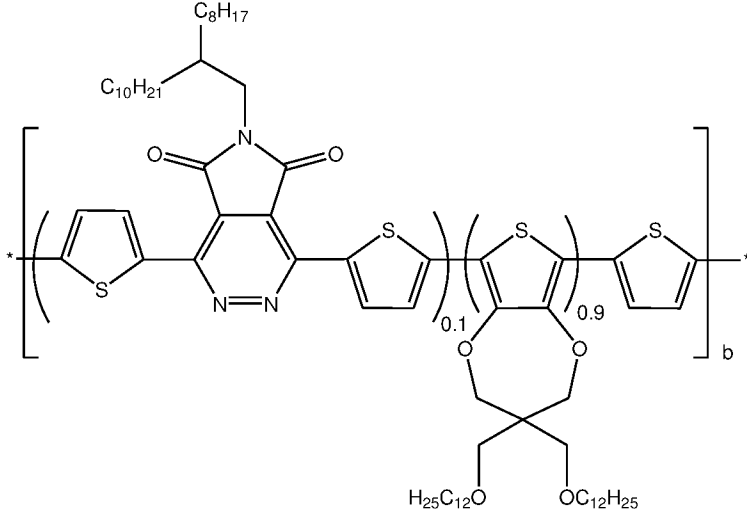
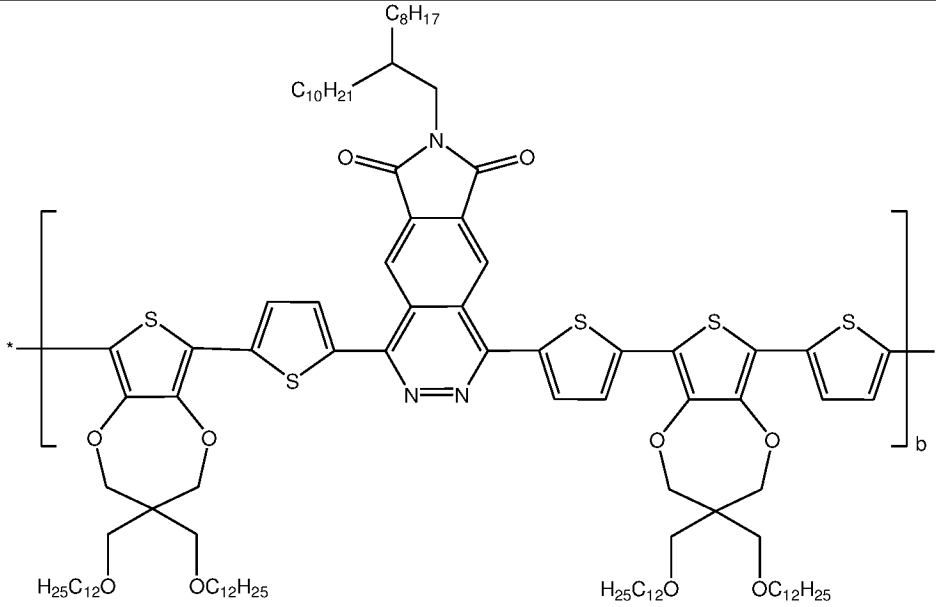
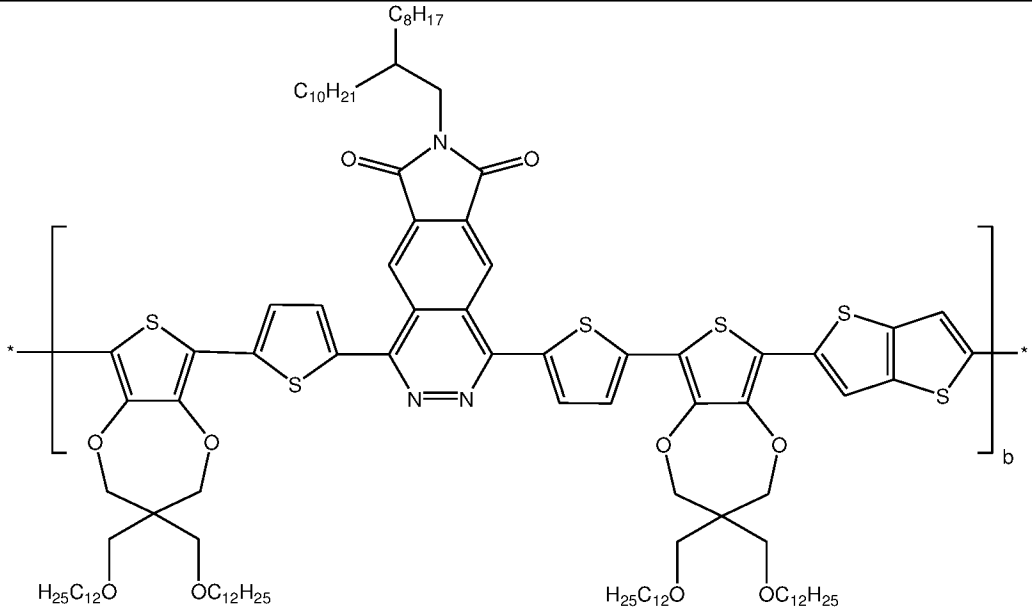
Monomer 12		butyl
Monomer 13		2-octyldodecyl

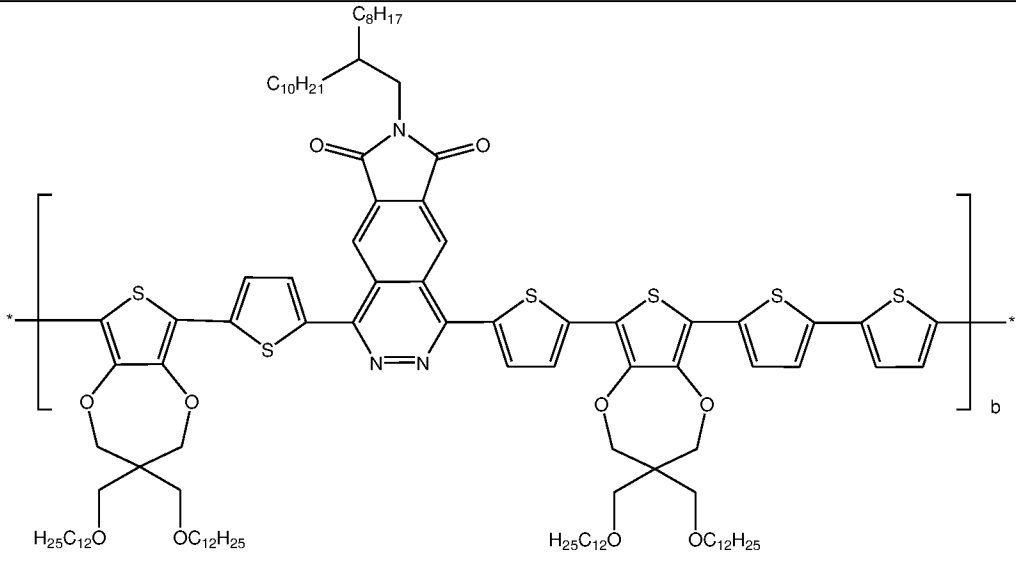
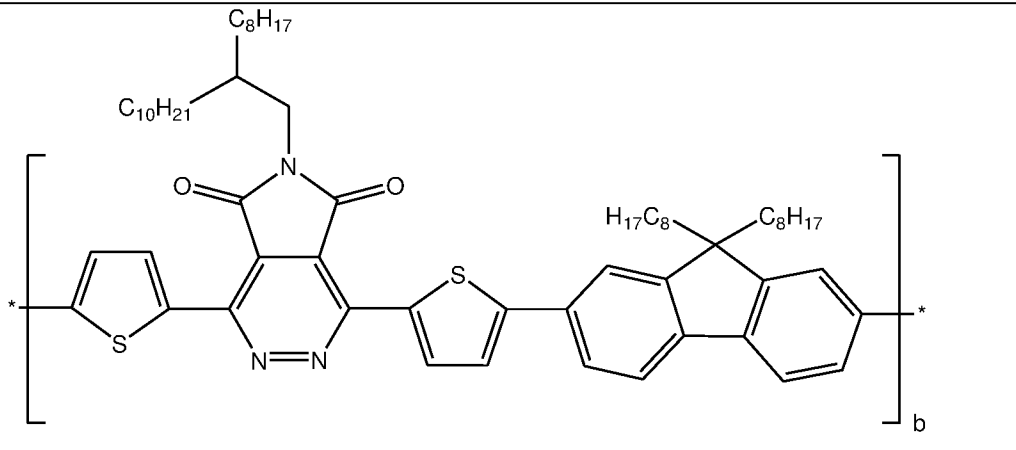
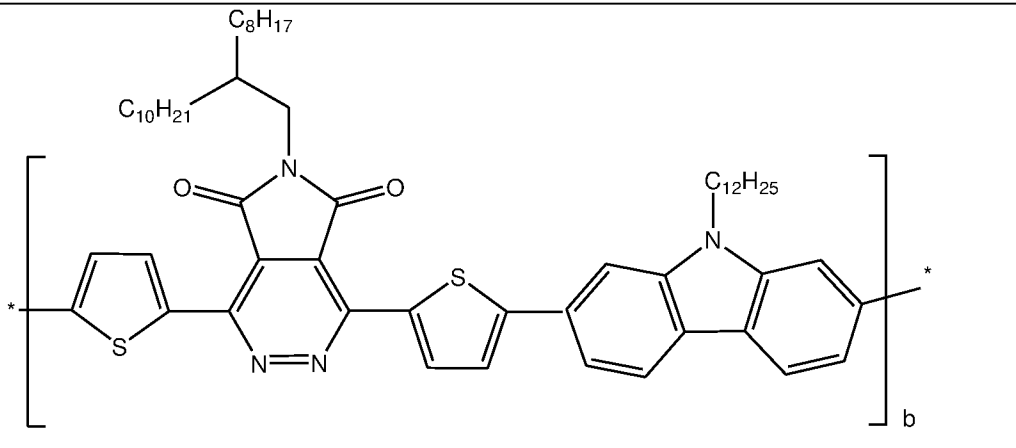
EXAMPLE 2

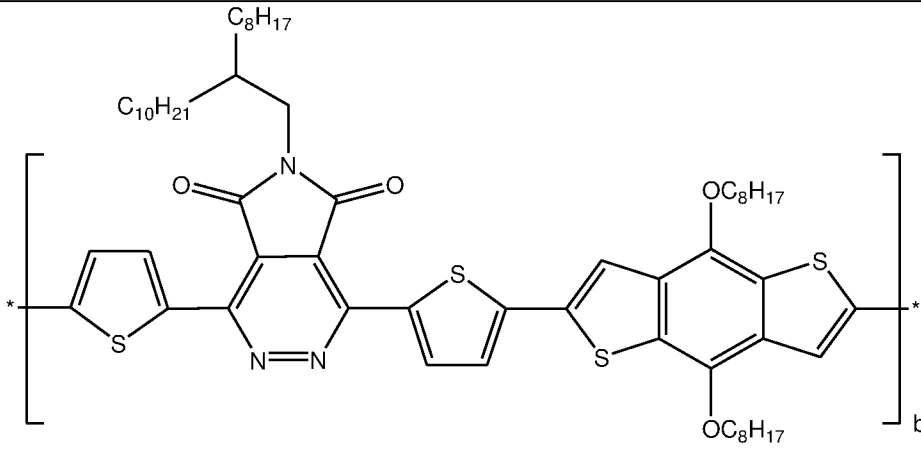
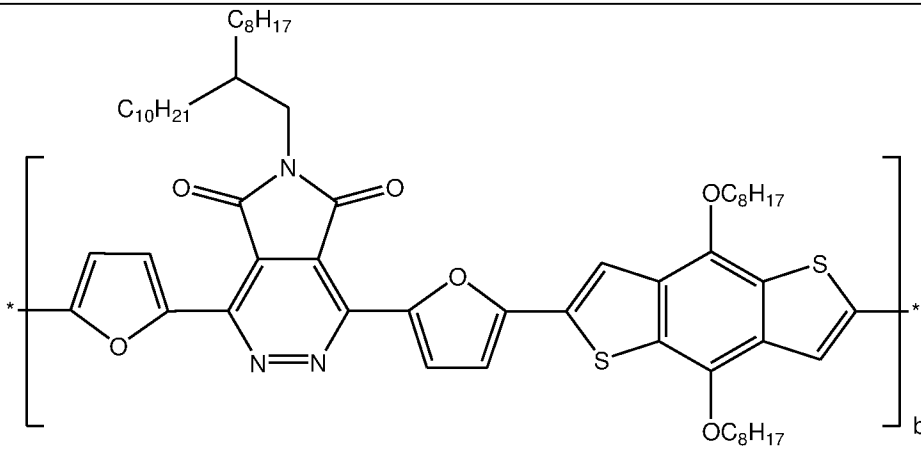
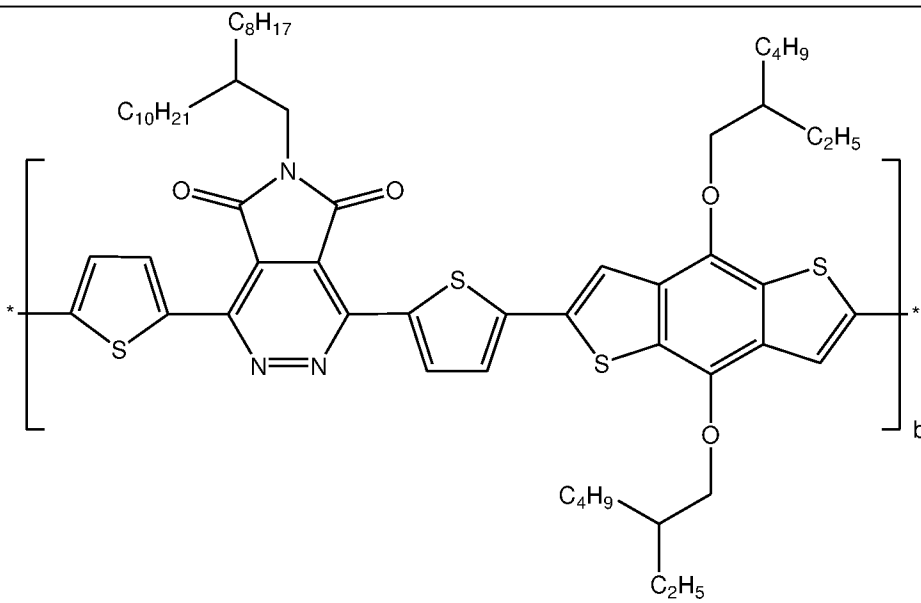
Some polymers synthesized from selected monomers in Tables 1 and 2 are shown in Table 3.

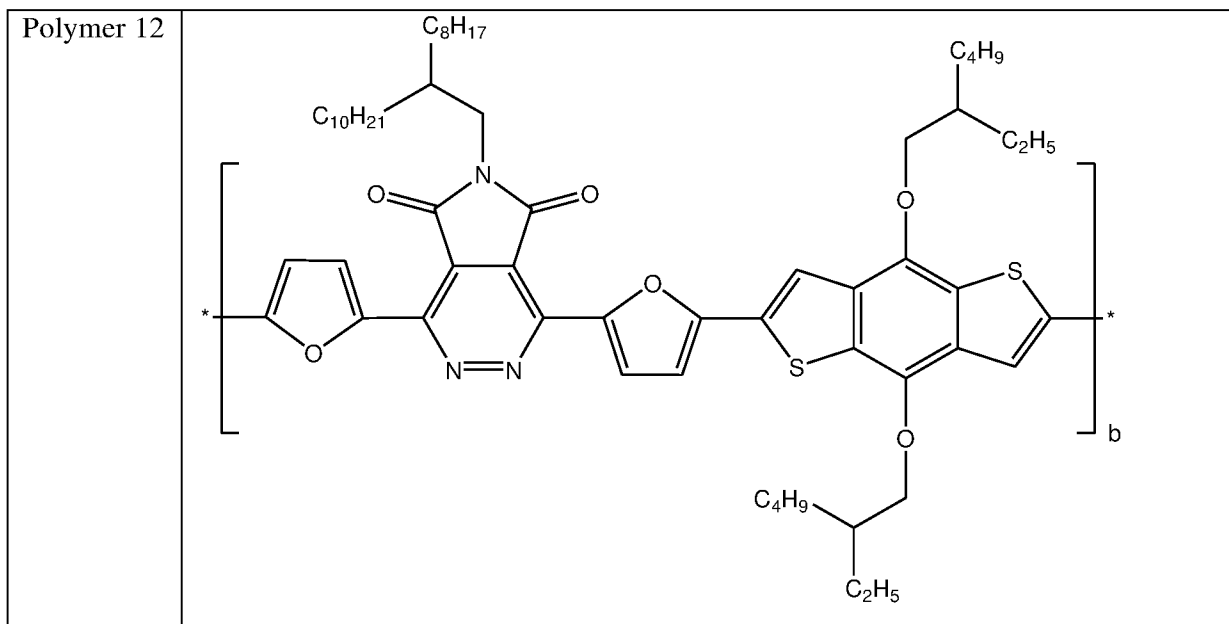
Table 3: Synthesized Polymers

Polymer 1	
Polymer 2	

Polymer 3	 Chemical structure of Polymer 3. The polymer consists of two repeating units, labeled with subscripts a and b. Unit a (enclosed in brackets with subscript a) is a 2,2'-bipyridine derivative where the 2,2'-positions are linked by a 1,3,4-oxadiazole ring. The 4,4'-positions of the bipyridine are linked to two thiophene rings. One thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The other thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. Unit b (enclosed in brackets with subscript b) is a 2,2'-bipyridine derivative where the 2,2'-positions are linked by a 1,3,4-oxadiazole ring. The 4,4'-positions of the bipyridine are linked to two thiophene rings. One thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The other thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The polymer is shown with a subscript a of 0.1 and a subscript b of 0.9.
Polymer 4	 Chemical structure of Polymer 4. The polymer consists of two repeating units, labeled with subscripts a and b. Unit a (enclosed in brackets with subscript a) is a 2,2'-bipyridine derivative where the 2,2'-positions are linked by a 1,3,4-oxadiazole ring. The 4,4'-positions of the bipyridine are linked to two thiophene rings. One thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The other thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. Unit b (enclosed in brackets with subscript b) is a 2,2'-bipyridine derivative where the 2,2'-positions are linked by a 1,3,4-oxadiazole ring. The 4,4'-positions of the bipyridine are linked to two thiophene rings. One thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The other thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The polymer is shown with a subscript a of 0.1 and a subscript b of 0.9.
Polymer 5	 Chemical structure of Polymer 5. The polymer consists of two repeating units, labeled with subscripts a and b. Unit a (enclosed in brackets with subscript a) is a 2,2'-bipyridine derivative where the 2,2'-positions are linked by a 1,3,4-oxadiazole ring. The 4,4'-positions of the bipyridine are linked to two thiophene rings. One thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The other thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. Unit b (enclosed in brackets with subscript b) is a 2,2'-bipyridine derivative where the 2,2'-positions are linked by a 1,3,4-oxadiazole ring. The 4,4'-positions of the bipyridine are linked to two thiophene rings. One thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The other thiophene ring is substituted with a 2,2,5-trimethyl-1,3-dioxane-5-carboxamide group, where the amide nitrogen is attached to a C_8H_{17} group and the carbonyl is attached to a $C_{10}H_{21}$ group. The polymer is shown with a subscript a of 0.1 and a subscript b of 0.9.

Polymer 6	 The structure of Polymer 6 is a block copolymer consisting of two units, 'a' and 'b', enclosed in brackets with asterisks at the ends. Unit 'a' is a 1,3-dioxolane ring substituted with a 2-ethylhexyl group (C₈H₁₇) and a decyl group (C₁₀H₂₁). Unit 'b' is a 1,3-dioxane ring substituted with a 2-ethylhexyl group (C₈H₁₇) and a dodecyl group (C₁₂H₂₅). The two units are linked by a central chain: a thiophene ring connected to a pyrazine ring, which is further connected to a thiophene ring, a 1,3-dioxane ring, a thiophene ring, and a 1,3-dioxolane ring.
Polymer 7	 The structure of Polymer 7 is a block copolymer consisting of two units, 'a' and 'b', enclosed in brackets with asterisks at the ends. Unit 'a' is a thiophene ring substituted with a 2-ethylhexyl group (C₈H₁₇) and a decyl group (C₁₀H₂₁). Unit 'b' is a fluorene ring substituted with a 2-ethylhexyl group (C₈H₁₇) and a dodecyl group (C₁₂H₂₅). The two units are linked by a central chain: a thiophene ring connected to a pyrazine ring, which is further connected to a thiophene ring, a 1,3-dioxane ring, a thiophene ring, and a 1,3-dioxolane ring.
Polymer 8	 The structure of Polymer 8 is a block copolymer consisting of two units, 'a' and 'b', enclosed in brackets with asterisks at the ends. Unit 'a' is a thiophene ring substituted with a 2-ethylhexyl group (C₈H₁₇) and a decyl group (C₁₀H₂₁). Unit 'b' is a fluorene ring substituted with a 2-ethylhexyl group (C₈H₁₇) and a dodecyl group (C₁₂H₂₅). The two units are linked by a central chain: a thiophene ring connected to a pyrazine ring, which is further connected to a thiophene ring, a 1,3-dioxane ring, a thiophene ring, and a 1,3-dioxolane ring.

Polymer 9	 The structure of Polymer 9 is a repeating unit enclosed in brackets with a subscript 'b'. It consists of a central pyrazine ring (N=N) connected at its 2 and 5 positions to two thiophene rings. The left thiophene ring is connected at its 2-position to a nitrogen atom of a five-membered imide ring. This imide ring has two carbonyl groups (C=O) and a side chain consisting of a methylene group, a chiral center (C) bonded to a C₈H₁₇ group and a C₁₀H₂₁ group, and another methylene group. The right thiophene ring is connected at its 2-position to a benzothienylene moiety, which is a benzene ring fused to a thiophene ring. This moiety has two OC₈H₁₇ groups at the 6 and 7 positions of the benzene ring. The 3-position of the thiophene ring in this moiety is connected to the polymer backbone, indicated by an asterisk (*).
Polymer 10	 The structure of Polymer 10 is a repeating unit enclosed in brackets with a subscript 'b'. It is similar to Polymer 9, but the thiophene rings are replaced by furan rings (oxygen instead of sulfur). The central pyrazine ring is connected at its 2 and 5 positions to two furan rings. The left furan ring is connected at its 2-position to a nitrogen atom of a five-membered imide ring, which has the same side chain as in Polymer 9. The right furan ring is connected at its 2-position to a benzothienylene moiety, which has two OC₈H₁₇ groups at the 6 and 7 positions of the benzene ring. The 3-position of the thiophene ring in this moiety is connected to the polymer backbone, indicated by an asterisk (*).
Polymer 11	 The structure of Polymer 11 is a repeating unit enclosed in brackets with a subscript 'b'. It is similar to Polymer 9, but the benzothienylene moiety on the right has two additional side chains. One side chain is an ether linkage (-O-) connected to a 1-butyl-2-ethyl ethoxy group (-CH₂CH(C₄H₉)CH₂CH₃). The other side chain is another ether linkage (-O-) connected to a 1-butyl-2-ethyl ethoxy group (-CH₂CH(C₄H₉)CH₂CH₃). The 3-position of the thiophene ring in this moiety is connected to the polymer backbone, indicated by an asterisk (*).



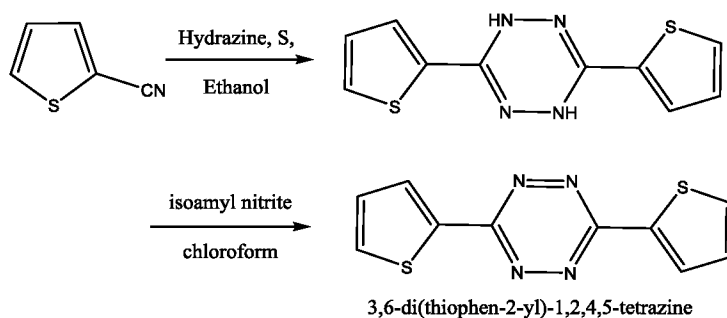
For all of polymers 1 to 12, b is an integer from 1 to 50.

EXAMPLE 3

Synthesis of the Tetrazine

- 5 The synthesis of a tetrazine precursor **1** is illustrated below:

3,6-Di(thiophen-2-yl)-1,2,4,5-tetrazine:



- 10 To a dried round bottom flask (1L) was added 2-cyanothiophene (50 grams, 0.4587 mol), hydrazine (30% concentration, 50 mL), sulphur powder (1.47 grams, 0.04587 mol) and ethanol (200 mL). The mixture was stirred at 70 °C for 3 hours before cooling down to room temperature. Brown crystals were formed at the bottom of the solution. The crystals were collected by suction filtration and washed with cold ethanol (100 mL). After complete drying, the collected crystal was loaded into a dry round bottom flask (1L). Isoamyl nitrite (107 grams, 0.9174 mol) and chloroform (200 mL) were
- 15 added into the round bottom flask. The mixture was stirred at room temperature for 6 hours. The solvent was removed by rotary evaporation and the remaining solid was recrystallized in toluene to afford the target compound as a pure red crystal. Yield = 47 grams, 84%.

EXAMPLE 4**Synthesis of Polymer 1, Polymer 2 and Polymer 3****General Synthesis of the Diels-Alder Product**

- 5 The general synthetic scheme for the monomer synthesis is provided in Fig. 1. A tetrazine (compound (I) in the detailed description, compound **1** in Fig. 1) was subjected to a Diels-Alder reaction with a dienophile. The dienophile may be a representative of the structure VIIa, as shown in compound **2** to yield compound **3**. The dienophile may be a representative of the structure VIIb, as shown in compound **4**, to yield compound **5**. Compound **5** may undergo a further elimination step, effected by treatment with N-bromo succinimide and dibenzoyl peroxide. A basic work-up then affords compound **6**. Compounds **3** and **6** may be further manipulated or used directly as monomers for the polymer synthesis.

Diels-Alder reaction – General Procedure for the synthesis of the compounds 3 and 5

- 15 To a dry round bottom flask was added the functionalized tetrazine compound (10mmol), the dienophile moiety (10mmol) and appropriate solvent. The solvent may be CHCl₃, DCM, THF, dioxane, toluene, chlorobenzene, dichlorobenzene, xylene, etc. The mixture was heated to reflux overnight. After it was cooled down, the mixture was poured into cold methanol and the precipitate was collected via suction filtration. It was then thoroughly washed with cold methanol and used directly for the next step without further purification.

20 **Elimination step- General Procedure for the synthesis of the compound 6**

- To a dry round bottom flask was added the substrate (8mmol), NBS (16mmol) and appropriate solvent (chloroform, tetrachloromethane, benzene etc.), benzoyl peroxide (1mmol). The mixture was heated to reflux overnight. After cooling down to room temperature, the mixture was poured into methanol. The precipitate was collected and used directly for the next step without further purification to yield the brominated product.

- To a dry round bottom flask was added the brominated product (4mmol), THF (10ml) and triethylamine (10ml). The mixture was stirred at room temperature overnight. The organic solvent was then removed and the target molecule was obtained by silica gel column chromatography.

30

The Stille Cross-Coupling Reaction for Polymer 1, Polymer 2 and Polymer 3

- 1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (24 mg, 0.032 mmol), 6,8-dibromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (200mg, 0.281 mmol), and 2,5-bis(trimethylstannyl)thiophene (128 mg, 0.312 mmol) were dissolved in 12ml of toluene. The mixture was stirred and purged with Argon for about 15 min, and then Pd(PPh₃)₄ (18.1 mg, 0.016 mmol) was added. The flask was purged with

35

Argon for another 15min before the mixture was heated to 110°C for 48hrs. Excess solvent was removed under reduced pressure and the polymer was precipitated with methanol. The suspension was filtered to give the crude product, which was then purified by Soxhlet extraction with acetone and chloroform. The chloroform fraction was evaporated to dryness to afford a purple-red solid.

The following stoichiometric ratio relative to 2,5-bis(trimethylstannyl)thiophene was used in the polymers:

Table 4: Stoichiometric ratios of starting material in Polymers 1, 2 and 3

	1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione	6,8-dibromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine
Polymer 1	0.5	0.5
Polymer 2	0.7	0.3
Polymer 3	0.9	0.1

EXAMPLE 5

Characterization of Polymer 1, Polymer 2 and Polymer 3

¹H NMR Characterization

Polymer 1. Yield 68%. ¹H NMR (main signals) (CDCl₃): δ 7.16-7.07 (br, s), 4.22 (br, s), 3.63-3.43 (br, m), 1.25 (br, s), 0.87 (br, s).

Polymer 2. Yield 70%. ¹H NMR (main signals) (CDCl₃): δ 7.06-7.00 (br, s), 4.16 (br, s), 3.62-3.42 (br, m), 1.25 (br, s), 0.88 (br, s).

Polymer 3. Yield 50%. ¹H NMR (main signals) (CDCl₃): δ 7.17-7.07 (br, s), 4.22 (br, s), 3.62-3.45 (br, m), 1.25 (br, s), 0.88 (br, s).

The GPC curves of these three polymers are shown in Fig. 2, 3 and 4. Gel permeation chromatography technique is commonly used to determine the molecular weight of the conjugated polymers. By reading the retention time of the polymer peak, the molecular weight can be determined according to the calibration data of some standard polymers.

UV-Vis Absorbance

The UV absorptions of solutions of the polymer 1, polymer 2 and polymer 3 in chlorobenzene in the wavelength range of 300 to 900 nm were recorded and are shown in Fig. 5.

EXAMPLE 6

Manufacture of Devices Using Polymer 1, Polymer 2 and Polymer 3

Indium tin oxide (ITO)/glass (15 Ω /sq, 35x30x1.1mm) were used as substrates. The substrates were cleaned by successive sonication in acetone, isopropyl alcohol and DI water for 15 minutes each. They were then blown dry using nitrogen gas. Polymer solutions of polymers 1-3 were prepared at a concentration of 10mg/ml using a mixed solvent system chloroform and chlorobenzene in a 6:4 volume ratio. The solutions were filtered through a 0.45 μ m PVDF syringe filter prior to use. 80 μ L of the polymer solution was pipetted onto the ITO/glass substrates and a polymer film was formed from spin-coating at 500 rpm for 60 seconds. The excessive polymer edges were removed by swabbing with chloroform using a cotton bud to obtain an active area of 2x2 cm². On a second piece of cleaned ITO/glass substrate, an area of 2x2 cm² was blocked out using parafilm. The total thickness of the parafilm spacer was kept constant at 0.01". 250 μ L of the gel electrolyte (0.512 g of lithium perchlorate and 2.8 g of poly(methyl methacrylate) (MW = 120 000 g/mol) in 6.65 ml of propylene carbonate and 28 ml of dry acetonitrile) was pipetted within the 2x2 cm² area and left to dry for 5 minutes.

The device was fabricated by assembling the two ITO/glass substrates together with the polymer film and gel electrolyte in contact. The device was secured using parafilm. A schematic depiction of the device thus produced is shown in Fig. 6. It shows the different layers of ITO/glass substrate with gel electrolyte and the polymer, as a top view (602) as well as a cross section (604). The ITO/glass substrate comprises the ITO/glass (610), polymer (612), parafilm (614) and gel electrolyte (616).

EXAMPLE 7

Characterization of Devices Manufactured Using Polymer 1, Polymer 2 and Polymer 3

UV-Vis absorbance

The UV-vis-NIR absorption spectra of the polymer devices at various applied potentials (V) for the polymer 1, polymer 2 and polymer 3 are recorded and shown in Fig. 7, Fig. 8 and Fig. 9. They demonstrate the dependence of the respective electronic transition states to an applied potential. When different voltage is applied on the polymer thin film, the film absorption the light differently and therefore there will be a color change on the color window of the electrochromic device.

Square-wave potential step absorbance

The square-wave potential step absorptiometry of the polymer devices between 1.5 V and -1.5 V with a switch time of 10 seconds were recorded for the polymer 1, polymer 2 and polymer 3 and shown in Fig. 10, Fig. 11 and Fig. 12. They demonstrate dependence of the respective electronic transition states to an applied potential and reversibility of the process. Switching time, bleaching time and the stability of the electrochromic device can be extracted from these data.

Optical and electrochemical properties

Fig. 13 shows photos of the polymer devices of the polymer 1, polymer 2 and polymer 3 in neutral state and under 2.0 V.

The optical and electrochemical properties of the polymers are shown in Table 5:

5 **Table 5. Optical and Electrochemical Properties of Polymers**

	λ_{max} , solution (nm)	λ_{onset} , solution (nm)	λ_{max} , film (nm)	λ_{onset} , film (nm)	Optical band gap (eV)	HOMO (eV)	LUMO (eV)
Polymer 1	532	713	530	732	1.74	-5.00	-3.26
Polymer 2	528	690	530	724	1.80	-4.95	-3.15
Polymer 3	533	660	544	699	1.88	-4.92	-3.04

The performance of the electrochromic devices in visible light is shown in Table 6.

Table 6. Performance of Electrochromic Devices in Visible light

	Contrast (%)	Bleaching Time (s)	Coloration Time (s)	Coloration Efficiency (cm ² /C)
Polymer 1	10.9 ± 0.1	8.30 ± 0.16	0.92 ± 0.07	331 ± 4
Polymer 2	12.4 ± 0.2	7.47 ± 0.39	0.87 ± 0.06	282 ± 15
Polymer 3	34.1 ± 0.51	7.62 ± 0.26	2.38 ± 0.24	436 ± 12

10 *Average values and standard deviations are reported based on 3 trials. Coloration refers to the process in which the percent transmittance changes from a higher value to a lower value. Bleaching refers to the process in which the percent transmittance changes from a lower value to a higher value.

The performance of the electrochromic devices in Near Infra Red (NIR) is shown in Table 7.

15 **Table 7. Performance of Electrochromic Devices in Near Infra Red (NIR)**

	Contrast (%)	Bleaching Time (s)	Coloration Time (s)	Coloration Efficiency (cm ² /C)
Polymer 1	36.2 ± 1.2	0.66 ± 0.11	8.06 ± 0.18	454 ± 35
Polymer 2	47.2 ± 1.5	0.85 ± 0.06	7.35 ± 0.14	453 ± 5
Polymer 3	54.2 ± 1.4	2.24 ± 0.24	7.12 ± 0.42	457 ± 14

*Average values and standard deviations are reported based on 3 trials. Coloration refers to the process in which the percent transmittance changes from a higher value to a lower value.

Bleaching refers to the process in which the percent transmittance changes from a lower value to a higher value.

EXAMPLE 8

5 Synthesis of Polymer 4, Polymer 5 and Polymer 6

General Synthetic Scheme

The general synthetic scheme is provided in Fig. 14, the following reactions are undertaken in order to make the polymer 4, polymer 5 and polymer 6.

Diels-Alder reaction (Synthesis of compound 9)

10 1,4-Bis(5-bromothiophen-2-yl)-7-(2-octyldodecyl)-5,5a,8a,9-tetrahydro-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (9).

To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (7) (3g, 7.43mmol), 2-(2-octyldodecyl)-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (8) (3.19g, 7.43mmol) and diphenyl ether (a) (20ml). The mixture was purged with argon for 15 min and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subjected to silica gel column chromatography. Hexane was first used to flush away the diphenyl ether. The target compound was then collected as yellow oil using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (5.10g, 82%). The product was contaminated by ca. 5% of starting material. The crude product was used for the next step without further purification. HR-APCI-MS: m/z = 804.1870, calculated exact mass: 804.1862, error: 0.9 ppm.

Elimination reaction (Synthesis of compound 10)

1,4-Bis(5-bromothiophen-2-yl)-7-(2-octyldodecyl)-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (10).

To a dry round bottom flask was added 1,4-bis(5-bromothiophen-2-yl)-7-(2-octyldodecyl)-5,5a,8a,9-tetrahydro-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (9) (1g, 1.25 mmol), NBS (b) (2.2 equiv. 490mg, 2.75mmol), benzoyl peroxide (0.1 equiv, 0.125mmol, 30mg) and dichloroethane (c) (20ml). The mixture was purged with argon for 15 min and then heated to 120 °C for 2 days. After cooling to room temperature, the solvent was removed by rotary evaporation. The residue was directly subjected to silica gel column chromatography to afford the target molecule as a yellow powder (720mg, 72%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.93 (s, 2H), 7.52-7.51 (d, 2H, J = 4 Hz), 7.28-7.27 (d, 2H, J = 4 Hz), 3.71-3.69 (d, 2H, J = 7.2 Hz), 1.94 (m, 1H), 1.29-1.23 (m, 32H), 0.88-0.84 (m, 6H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 166.84, 152.67, 140.05, 134.21, 131.63, 131.41, 127.56, 122.31, 119.06, 43.60, 37.41, 32.28, 31.89, 30.33, 30.02, 29.69, 26.66, 23.06, 14.50. HR-EI-MS: m/z = 801.1470, calculated exact mass: 801.1456, error: 1.81 ppm.

The ¹H NMR, ¹³C NMR and HRMS spectra of this compound (compound 10) are provided in Fig. 15, Fig. 16 and Fig. 17, respectively.

Cross-Coupling reaction (Synthesis of compound 12)**1,4-Bis(5-(3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)thiophene-2-yl)-7-(2-octyldodecyl)-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (12).**

To a dry round bottom flask was added (3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)trimethylstannane (11) (2 g, 50% purity), 1,4-bis(5-bromothiophen-2-yl)-7-(2-octyldodecyl)-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (10) (370mg, 0.47 mmol), Pd(PPh₃)₄ (0.1 equiv, 0.047 mmol, 54 mg) and dry toluene (15ml). The mixture was degassed by purging with argon and then heated to 110 °C for 16h. After cooling to room temperature, the solvent was removed by rotary evaporation. The collected residue was dissolved in minimum amount of chloroform and directly subjected to silica gel column chromatography. The target compound was then collected as red waxy solid using a solvent mixture (Hex:CHCl₃ = 1:1) (510mg, 62%). The target compound was found to be unstable at ambient condition. It was stored in the fridge after preparation. ¹H NMR (400 MHz, CDCl₃): δ ppm = 9.00 (s, 2H), 7.68 (d, 2H, J = 3.6 Hz), 7.38-7.37 (d, 2H, J = 4 Hz), 6.45 (s, 2H), 4.22 (s, 4H), 4.10 (s, 4H), 3.71-3.69 (d, 2H, J = 7.2 Hz), 3.55 (m, 8H), 3.44-3.41 (m, 8H), 1.94 (m, 1H), 1.68 (m, 4H), 1.56-1.54 (m, 8H), 1.30-1.24 (m, 100H), 0.88-0.85 (m, 18H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 167.06, 152.76, 150.41, 147.06, 141.15, 136.18, 134.00, 131.31, 127.99, 123.98, 122.81, 116.59, 103.85, 74.41, 72.20, 70.00, 48.25, 43.53, 37.41, 32.33, 31.89, 30.36, 30.08, 29.97, 29.77, 26.58, 23.09, 14.52. HR-APCI-MS: m/z = 1744.1423, calculated exact mass: 1744.1411, error: 0.67 ppm.

Bromination reaction (Synthesis of compound 13)**1,4-Bis(5-(8-bromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-7-(2-octyldodecyl)-6H-pyrrolo[3,4-g]-phthalazine-6,8(7H)-dione (13).**

To a dry round bottom flask was added 1,4-Bis(5-(3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)thiophene-2-yl)-7-(2-octyldodecyl)-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (12) (1 g, 0.573 mmol), NBS (b) (2.2 equiv., 1.26mmol, 225mg) and chloroform (10ml). The mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation and the residue was directly subjected to silica gel chromatography using hexane: chloroform (1:1) to afford the target product as a red waxy solid (0.92g, 85%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.98 (s, 2H), 7.66-7.65 (d, J = 4 Hz, 2H), 7.30-7.29 (d, J = 4 Hz, 2H), 4.22 (s, 4H), 4.17 (s, 4H), 3.71-3.69 (d, J = 7.2 Hz, 2H), 3.55 (s, 8H), 3.44-3.41 (t, J = 6.4 Hz, 8H), 1.91 (m, 1H), 1.55-1.24 (m, 112H), 0.88-0.85 (m, 18H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 167.02, 152.76, 148.45, 145.93, 139.98, 133.99, 131.14, 127.78, 124.09, 123.11, 122.72, 116.27, 92.92, 74.67, 72.19, 69.90, 48.31, 43.53, 37.43, 32.31, 31.89, 30.35, 30.09, 26.60, 23.11, 14.54. HR-APCI-MS: m/z = 1901.9589, calculated exact mass: 1901.9568, error: 1.17 ppm.

Stille cross-coupling polymerization.

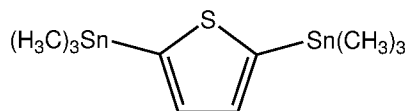
1,4-Bis(5-(8-bromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-7-(2-octyldodecyl)-6H-pyrrolo[3,4-g]-phthalazine-6,8(7H)-dione (13) (300mg, 0.158 mmol) and bis(trimethylstannyl) compounds 14 (0.158 mmol) were dissolved in 10 ml of toluene. The mixture was stirred and purged with argon for about 15 min, and then Pd(PPh₃)₄ (6% equiv., 0.00948mmol, 11mg) was added. The flask was purged with argon for another 15 min before the

mixture was heated to 110 °C for 2 days. Excess solvent was removed under reduced pressure and the polymer was precipitated with methanol. The suspension was filtered to give the crude product, which was then purified by Soxhlet extraction with acetone and chloroform. The chloroform fraction was evaporated to dryness to afford the target polymer materials 15.

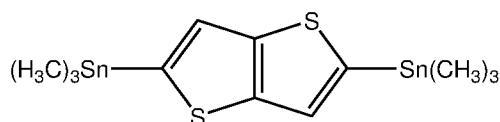
5

The bis(trimethylstannyl) compounds 14 were as follows:

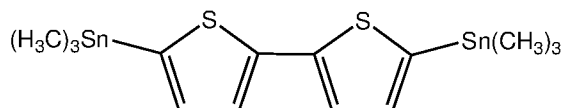
Polymer 4:



Polymer 5:



Polymer 6:



EXAMPLE 9

Characterization of Polymer 4, Polymer 5 and Polymer 6

10 ¹H NMR Characterization

Polymer 4. Yield 74%. ¹H NMR (main signals) (CDCl₃): δ 9.09 (br), 7.92 (br), 4.31 (br, m), 3.72-3.45 (br, m), 1.68-1.58 (br, m), 1.24 (m), 0.87 (m).

Polymer 5. Yield 72%. ¹H NMR (main signals) (CDCl₃): δ 8.99 (br), 7.65 (br), 4.33 (br), 3.62-3.48 (br, m), 1.24 (br, m), 0.86 (br, m).

15 **Polymer 6.** Yield 55%. ¹H NMR (main signals) (CDCl₃): δ 9.08 (br), 7.82 (br), 6.97 (br), 4.31(br), 3.70-3.48 (br, m), 1.79-1.68 (br), 1.24 (br), 0.86(br).

The ¹H NMR spectra of these Polymer 4, Polymer 5 and Polymer 6 are provided in Fig. 18, Fig. 19 and Fig. 20, respectively.

20 **EXAMPLE 10**

Manufacture of Devices Using Polymer 4, Polymer 5 and Polymer 6

Prior to use, ITO/glass substrates were cleaned by successive ultrasonication in acetone, isopropyl alcohol and distilled water, and blown dry with N₂. Polymer solutions of polymer 4, polymer 5 and polymer 6 were prepared at a concentration of 15 mg/mL in 6:4 (v/v) chloroform:chlorobenzene mixed solvent. Warm polymer solution (50 °C) was filtered and spin-coated onto the heated ITO substrates (50 °C) at 1200 rpm for 60 seconds to yield film thickness of around 100 nm. For drop-cast films, the polymer solutions are dispensed, spread onto the ITO substrates and left to dry. Film thickness of approximately 150-200 nm was

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obtained. Excessive polymer edges were removed by swabbing with chloroform using a cotton bud to obtain an active area of $2 \times 2 \text{ cm}^2$. On a second piece of ITO substrate, an area of $2 \times 2 \text{ cm}^2$ was blocked out using parafilm. The total thickness of the parafilm spacer and barrier was kept constant at 0.01". 250 μL of the gel electrolyte (0.512 g of lithium perchlorate and 2.8 g of poly(methyl methacrylate) (MW = 120 000 g/mol) in 6.65 ml of propylene carbonate and 28 ml of dry acetonitrile) was pipetted within the $2 \times 2 \text{ cm}^2$ area. The device was fabricated by assembling the two ITO/glass substrates together with the polymer film and gel electrolyte in contact.

EXAMPLE 11

Characterization of Devices Manufactured Using Polymer 4, Polymer 5 and Polymer 6

Electron capture (EC) electrospectroscopy

The electron capture (EC) electrospectroscopy of the polymer 5 in a EC device is depicted in Fig. 21.

Fig 21 describes the UV-vis-NIR absorption behavior of polymer P5 electrochromic device upon oxidative voltage bias. When no voltage is applied on the polymer film, the polymer mainly absorbs around 500 nm and the neutral polymer film has a dark purple color. When an intermediate voltage is applied to the thin film, e.g., 1.5 V, the partially oxidized polymer film mainly absorbs around 800 nm. At this voltage, the thin film color is changed to light brown. When even higher voltage is applied at 2.0 V, the absorption of the polymer in the visible light region (400 – 700 nm) is depleted. The polymer film at 2.0 V mainly absorbs in the NIR region with a broad peak at 1200 nm. The polymer thin film then appears to be light cyan-colored. This indicates that the polymer can be used as a useful material for color-switching smart window applications.

The electrochromic performance of the polymer devices of Polymer 4, Polymer 5 and Polymer 6 are summarized in the following Table 8:

Table 8: Electrochromic performance of Devices Comprising Polymers 4, 5 and 6

	Optical contrast (%)		Bleaching time (s)		Coloration time (s)		CE (cm^2/C)	
	λ_{max}	1400 nm	λ_{max}	1400 nm	λ_{max}	1400 nm	λ_{max}	1400 nm
Polymer 4	11	58	23.2	17.6	4.0	23.6	205	379
Polymer 5	34	71	23.0	2.59	1.8	17.7	471	651
Polymer 6	14	62	25.3	17.9	4.5	23.6	274	366

The optical contrast refers to how much the color of the film has changed upon an applied voltage. Polymers 4, 5 and 6 showed reasonably good optical contrast in the visible region and good contrast in the NIR region. The bleaching time and coloration time refer to how fast the

device changes its color. Polymers 4, 5 and 6 showed good coloration time below 5 seconds. This means that upon an applied voltage, the thin film device will reach their full optical contrast in less than 5 seconds. The coloration efficiency describes how much electricity is needed to power the polymer device. The coloration efficiency for this batch of polymers is generally good with values greater than 200 cm²/C.

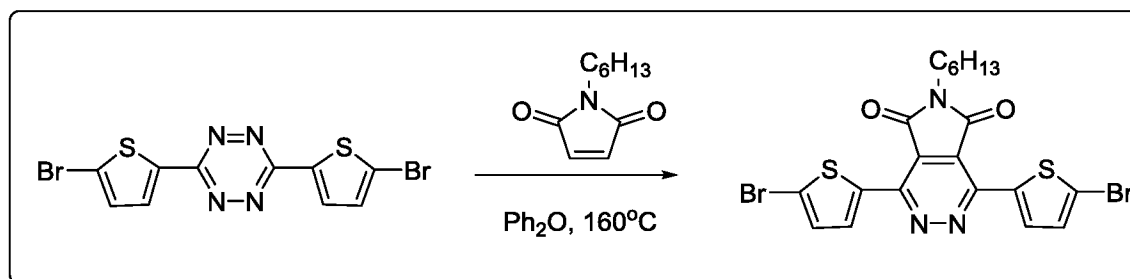
EXAMPLE 12

Time-Dependent Density Functional Theory Calculation

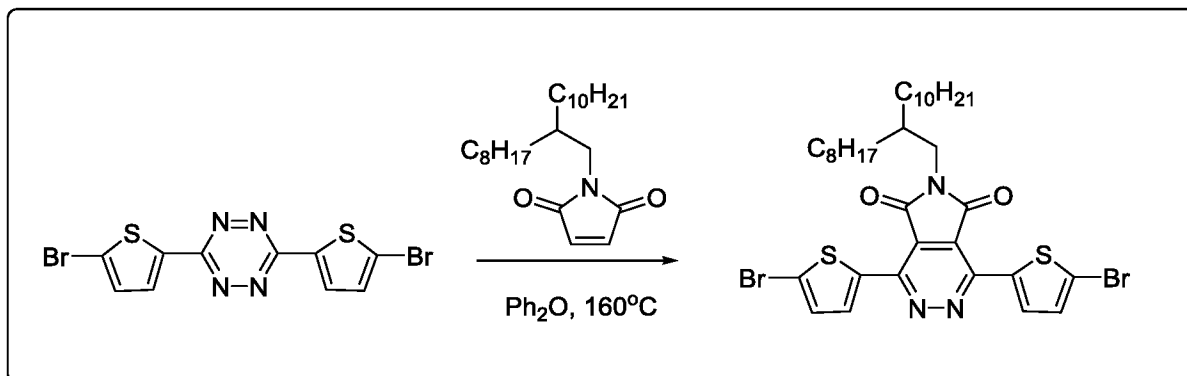
Time-dependent density-functional theory calculation is carried out to compare the magnitude of electron deficiency of the imide-fused pyridazines with current commonly used electron deficient acceptors. The results shown in Fig. 22 revealed that all widely used monomers, such as dikeftopyrrolopyrrole (DPP), benzotriazole (BT), iso-indigo, tetrazine, etc have lower electron-deficiency than imide-fused pyridazines synthesized according to the present disclosure. There is only one known electron-deficient acceptor benzo(bis)thiadiazole (BBT) which has higher electron deficiency than the imide-fused pyridazines of the present disclosure. However, BBT has no suitable position to undergo further functionalization, and hence BBT-based polymers typically have poor solubility in solvents. In contrast, imide-fused pyridazine can be conveniently functionalized with flexible alkyl chains to enhance its processability, making it more promising to integrate with other donors to prepare more processable polymers.

EXAMPLE 13

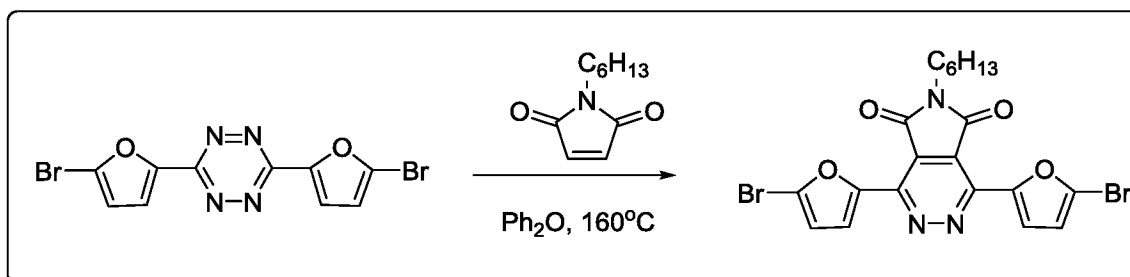
Monomer 1:



1,4-Bis(5-bromothiophen-2-yl)-6-hexyl-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione: To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (300 mg, 0.743 mmol), 1-(2-hexyl)-1H-pyrrole-2,5-dione (135 mg, 0.743 mmol) and diphenyl ether (10ml). The mixture was purged with argon for 15 min and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (230 mg, 56%). ¹H NMR (400 MHz, CDCl₃): δ ppm =8.62-8.61 (d, *J* = 4 Hz, 2H), 7.20-7.18 (d, *J* = 3.6 Hz, 2H), 3.79-3.76 (t, *J* = 7.6 Hz, 2H), 1.72-1.67 (m, 2H), 1.33 (m, 6H), 0.91-0.87 (t, *J* = 6.4 Hz, 3H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 167.47, 148.32, 139.74, 134.33, 132.09, 122.57, 121.47, 39.64, 31.66, 28.58, 26.92, 22.87, 14.40. HR-EI-MS: *m/z* = 552.9136, calculated exact mass: 552.9123, error: 2.28 ppm.

Monomer 3:**5 1,4-Bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione:**

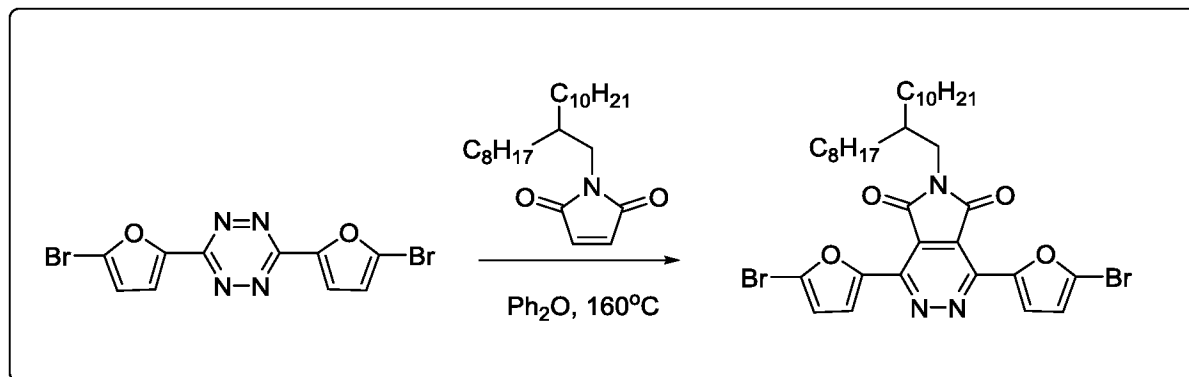
To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (3g, 7.43 mmol), 1-(2-octyldodecyl)-1H-pyrrole-2,5-dione (2.8g, 7.43 mmol) and diphenyl ether (20ml). The mixture was purged with argon for 15 min and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (3.42g, 62%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.63-8.62 (d, *J* = 4 Hz, 2H), 7.19-7.18 (d, *J* = 4 Hz, 2H), 3.67-3.65 (d, *J* = 7.2 Hz, 2H), 1.90 (m, 1H), 1.25-1.24 (m, 32H), 0.89-0.85 (m, 6H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 167.72, 148.30, 139.78, 134.38, 132.09, 122.47, 121.47, 43.81, 37.37, 32.31, 32.27, 31.85, 30.31, 30.02, 29.97, 29.93, 29.75, 29.68, 26.62, 23.08, 14.52. HR-EI-MS: *m/z* = 750.1408, calculated exact mass: 750.1393, error: -2.1 ppm.

Monomer 4:

20 1,4-Bis(5-bromofuran-2-yl)-6-hexyl-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione: To a dry round bottom flask was added 3,6-bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine (300 mg, 0.81 mmol), 1-(2-hexyl)-1H-pyrrole-2,5-dione (146 mg, 0.81 mmol) and diphenyl ether (10ml). The mixture was purged with argon for 15 min and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (310 mg, 73%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.03- 8.02 (d, *J* = 3.6 Hz, 2H), 6.62-6.61 (d, *J* = 4 Hz, 2H), 3.77-3.73 (t, *J* = 7.6 Hz, 2H), 1.70-1.65

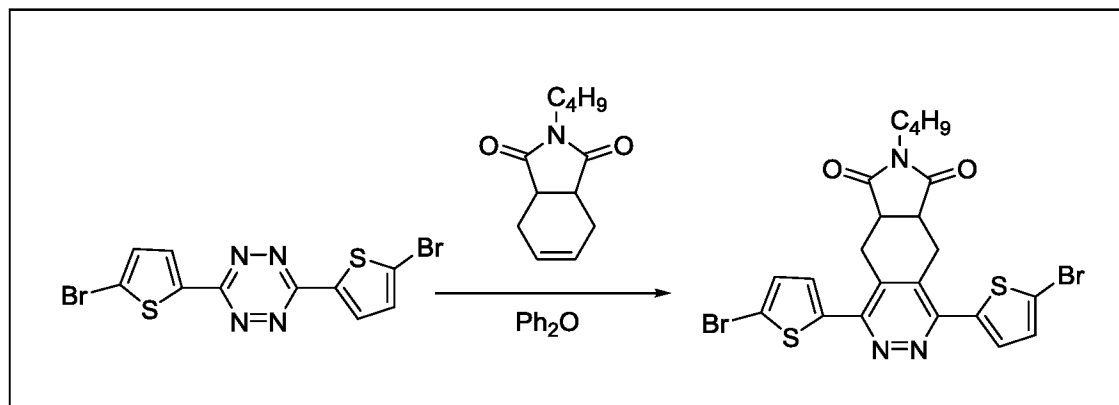
(m, 2H), 1.32 (m, 6H), 0.89-0.86 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3): δ ppm = 167.72, 148.30, 139.78, 134.38, 132.09, 122.47, 121.47, 43.81, 37.37, 32.31, 32.27, 31.85, 30.31, 30.02, 29.97, 29.93, 29.75, 29.68, 26.62, 23.08, 14.52. HR-EI-MS: $m/z = 520.9586$, calculated exact mass: 520.9580, error: 1.04 ppm.

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Monomer 6:

1,4-Bis(5-bromofuran-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione: To a dry round bottom flask was added 3,6-bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine (1.48g, 4 mmol), 1-(2-octyldodecyl)-1H-pyrrole-2,5-dione (4 mmol, 1.51g) and diphenyl ether (15ml). The mixture was degassed by purging with argon and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex: CHCl_3 =1:1) then CHCl_3 as eluent (1.86g, 65%). ^1H NMR (400 MHz, CDCl_3): δ ppm = 8.06 (d, 2H, $J = 3.6$ Hz), 6.64-6.63 (d, 2H, $J = 3.6$ Hz), 3.66-3.64 (d, 2H, $J = 7.6$ Hz), 1.57 (m, 1H), 1.24 (m, 32H), 0.89-0.85 (m, 6H). ^{13}C NMR (100MHz, CDCl_3): δ ppm = 166.89, 149.69, 143.31, 128.45, 122.25, 121.37, 115.17, 43.77, 37.29, 32.30, 31.81, 30.30, 30.01, 29.73, 29.67, 26.59, 23.07, 14.51. HR-EI-MS: $m/z = 719.1476$, calculated exact mass: 719.1756, error: -1.41 ppm.

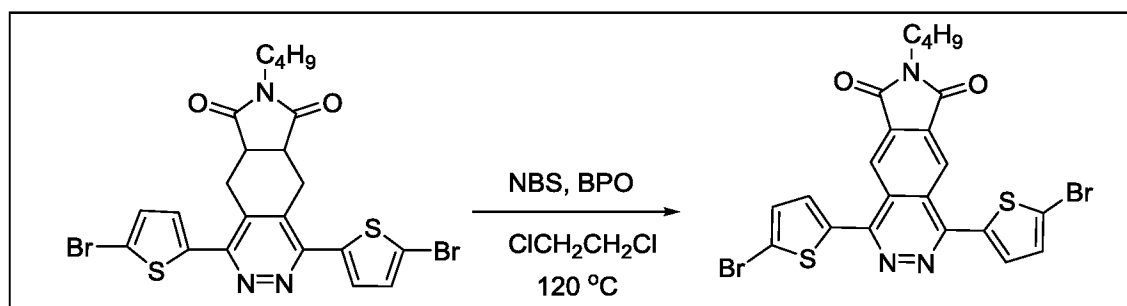
20

Monomer 10 – step 1:

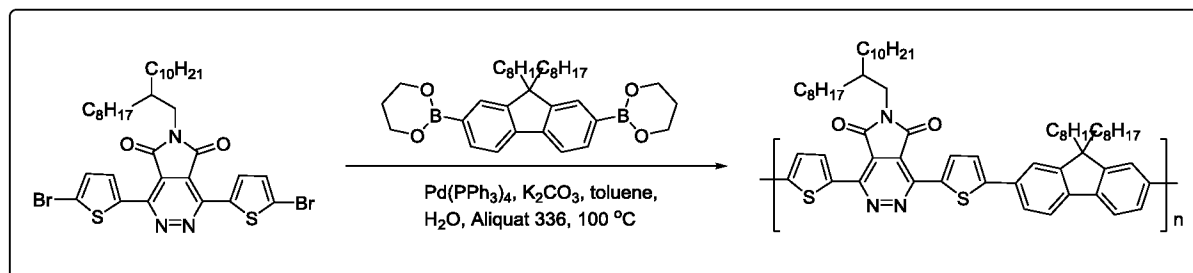
1,4-Bis(5-bromothiophen-2-yl)-7-butyl-5,5a,8a,9-tetrahydro-6H-pyrrolo[3,4-g]phthalazine-

6,8(7H)-dione: To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (400mg, 0.1 mmol), 2-butyl-3a,4,7,7a-tetrahydro-1H-isoindole 1,3(2H)-dione (207mg, 0.1mmol) and diphenyl ether (10ml). The mixture was purged with argon for 15 min and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (410mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 7.32-7.31 (d, *J* = 4 Hz, 2H), 7.16-7.15(d, *J* = 4 Hz, 2H), 3.83-3.79 (m, 2H), 3.44-3.42 (m, 2H), 3.38-3.35 (t, *J* = 6.8 Hz, 2H), 2.94-2.90 (m, 2H), 1.27-1.22 (m, 2H), 0.74-0.70 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 178.33, 151.97, 140.45, 133.24, 131.26, 129.88, 117.50, 39.39, 38.88, 29.69, 25.21, 19.85, 13.80. HR-EI-MS: *m/z* = 580.9288, calculated exact mass: 580.9265, error: 3.94 ppm.

The HR-EI MS spectrum for this intermediate is shown further below as Fig. 22.

Monomer 10 – step 2:

1,4-Bis(5-bromothiophen-2-yl)-7-butyl-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione: To a dry round bottom flask was added 1,4-bis(5-bromothiophen-2-yl)-7-butyl-5,5a,8a,9-tetrahydro-6H-pyrrolo[3,4-g]phthalazine-6,8(7H)-dione (200mg, 0.345mmol), NBS (2.2 equiv., 0.76 mmol, 135mg), BPO (0.1 equiv. 0.0345mol, 10mg) and dichloroethane (10ml). The mixture was purged with argon for 10min and then heated to 120 °C for 2 days. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Chloroform was used as the eluent and the target product was obtained as a yellow solid. (135mg, 68%) ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.92 (s, 2H), 7.52-7.51 (d, *J* = 4 Hz, 2H), 7.29-7.28 (d, *J* = 3.6 Hz, 2H), 3.83-3.80 (t, *J* = 7.2 Hz, 2H), 1.76-1.68 (m, 2H), 1.45-1.37 (m, 2H), 0.99-0.95 (t, *J* = 7.6 Hz, 3H) ¹³C NMR (100MHz, CDCl₃): δ ppm = 166.52, 152.63, 139.69, 134.39, 131.69, 131.61, 127.66, 122.35, 119.26, 39.14, 30.82, 20.49, 14.00. HR-EI-MS: *m/z* = 572.8961, calculated exact mass: 576.8952, error: 1.65 ppm.

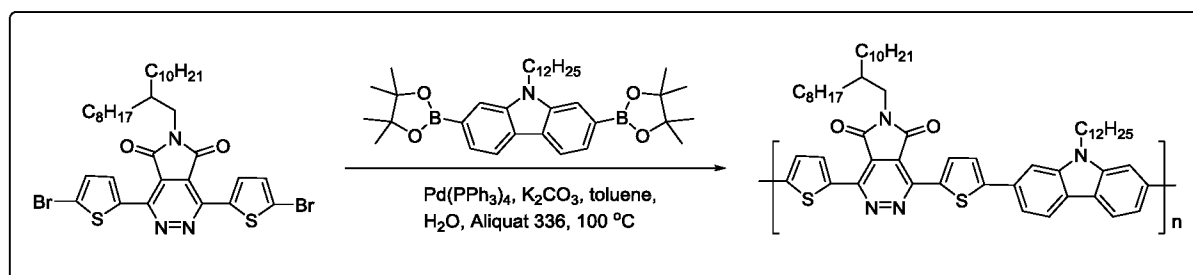
EXAMPLE 14**Further Experimental Examples relating to the Polymer Syntheses****Polymer 7:**

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To a dry round bottom flask was added 1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (225mg, 0.3mmol), 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (168mg, 0.3mmol), $\text{Pd(PPh}_3)_4$ (6mol%, 0.018mmol, 21mg), K_2CO_3 (2mmol, 276mg), H_2O (1ml), toluene (10ml) and Aliquat 336 (catalytic amount). The mixture was purged with argon for 30min and then heated to $100\text{ }^\circ\text{C}$ for 48h. After cooling to room temperature, chloroform was added to dilute the solution and then extraction with water was done for three times. The organic layer was collected and dried by rotary evaporation. The residue was dissolved in minimal amount of chloroform and precipitated into methanol solution. The red precipitate was collected via suction filtration. The polymer was purified by Soxhlet extraction with hexane for 20h, followed by acetone for 20h and finally washed down by chloroform. The chloroform part was concentrated and dropped into methanol solution with rigorous stirring. The precipitate was collected via suction filtration, thoroughly washed with methanol and dried under vacuum. (250mg, 85%)

10

15

Polymer 8:

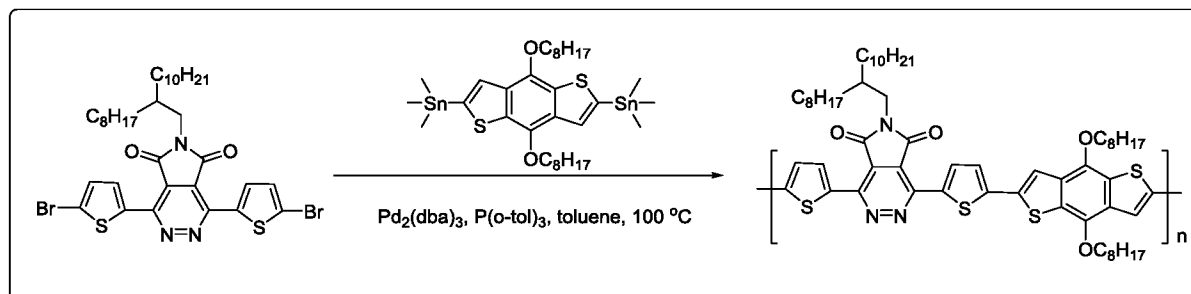
20

To a dry round bottom flask was added 1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (225mg, 0.3mmol), 9-(2-dodecyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (210mg, 0.3mmol), $\text{Pd(PPh}_3)_4$ (6mol%, 0.018mmol, 21mg), K_2CO_3 (2mmol, 276mg), H_2O (1ml), toluene (10ml) and Aliquat 336 (catalytic amount). The mixture was purged with argon for 30min and then heated to $100\text{ }^\circ\text{C}$ for 48h. After cooling to room temperature, chloroform was added to dilute the solution and then extraction with water was done for three times. The organic layer was collected and dried by rotary evaporation. The residue was dissolved in minimal amount of chloroform and precipitated into methanol solution. The

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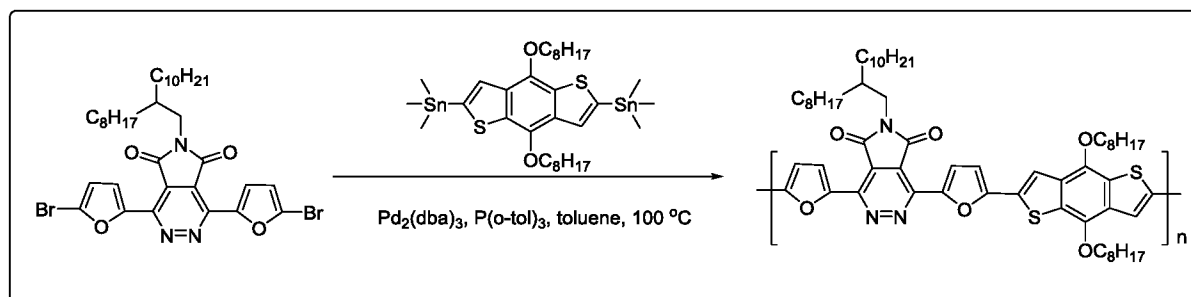
purple precipitate was collected via suction filtration. The polymer was purified by Soxhlet extraction with hexane for 20h, followed by acetone for 20h and finally washed down by chloroform. The chloroform part was concentrated and dropped into methanol solution with rigorous stirring. The precipitate was collected via suction filtration, thoroughly washed with methanol and dried under vacuum. (250mg, 85%)

Polymer 9:



To a dry round bottom flask was added 1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (225mg, 0.3mmol), (4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (232 mg, 0.3mmol), $\text{Pd}_2(\text{dba})_3$ (3 mol%, 0.009mmol, 8.5mg), $\text{P}(\text{o-tol})_3$ (12 mol%, 0.036mmol, 11 mg) and toluene (10ml). The mixture was purged with argon for 30min and then heated to 100 °C for 16h. After cooling to room temperature, chloroform was added to dilute the solution and then extraction with water was done for three times. The organic layer was collected and dried by rotary evaporation. The residue was dissolved in minimal amount of chloroform and precipitated into methanol solution. The precipitate was collected via suction filtration. The polymer was purified by Soxhlet extraction with hexane for 20h, followed by acetone for 20h and finally washed down by chloroform. The chloroform part was concentrated and dropped into methanol solution with rigorous stirring. The precipitate was collected via suction filtration, thoroughly washed with methanol and dried under vacuum. (230mg, 74%)

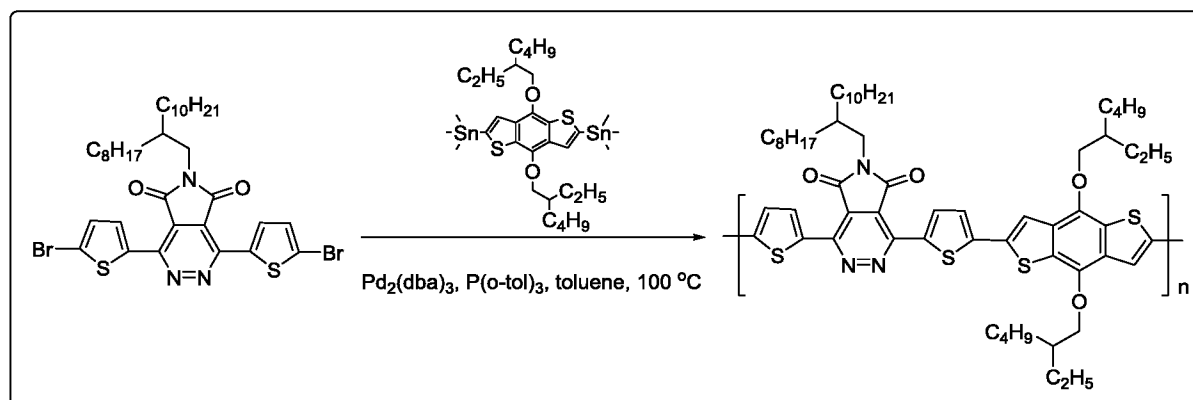
Polymer 10:



To a dry round bottom flask was added 1,4-bis(5-bromofuran-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (216mg, 0.3mmol), (4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (232 mg, 0.3mmol), $\text{Pd}_2(\text{dba})_3$ (3 mol%, 0.009mmol, 8.5mg), $\text{P}(\text{o-tol})_3$ (12 mol%, 0.036mmol, 11 mg) and toluene (10ml). The mixture was purged with argon for 30min and then heated to 100 °C for 16h. After cooling to room temperature, chloroform

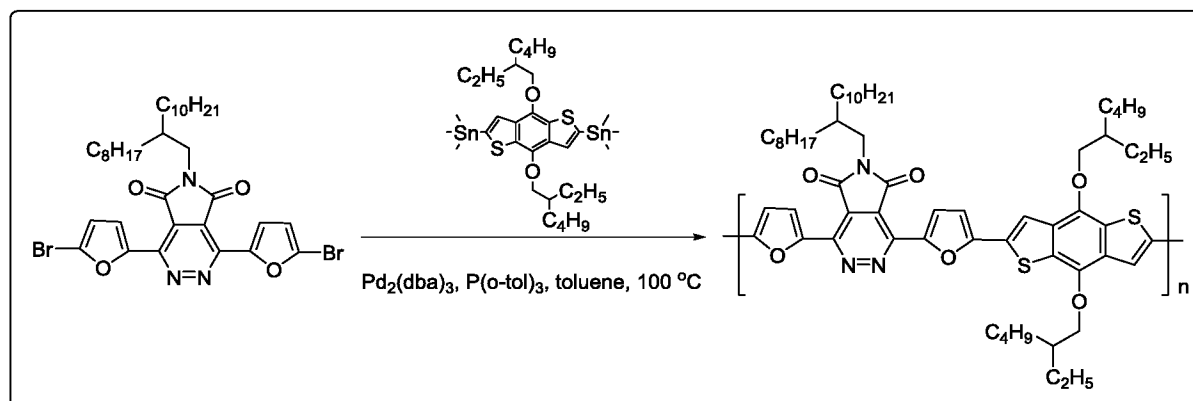
was added to dilute the solution and then extraction with water was done for three times. The organic layer was collected and dried by rotary evaporation. The residue was dissolved in minimal amount of chloroform and precipitated into methanol solution. The precipitate was collected via suction filtration. The polymer was purified by Soxhlet extraction with hexane for 20h, followed by acetone for 20h and finally washed down by chloroform. The chloroform part was concentrated and dropped into methanol solution with rigorous stirring. The precipitate was collected via suction filtration, thoroughly washed with methanol and dried under vacuum. (215mg, 72%)

Polymer 11:



To a dry round bottom flask was added 1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (225mg, 0.3mmol), 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diylbis(trimethylstannane) (232 mg, 0.3mmol), $\text{Pd}_2(\text{dba})_3$ (3 mol%, 0.009mmol, 8.5mg), $\text{P}(\text{o-tol})_3$ (12 mol%, 0.036mmol, 11 mg) and toluene (10ml). The mixture was purged with argon for 30 min and then heated to $100\text{ }^\circ\text{C}$ for 16h. After cooling to room temperature, chloroform was added to dilute the solution and then extraction with water was done for three times. The organic layer was collected and dried by rotary evaporation. The residue was dissolved in minimal amount of chloroform and precipitated into methanol solution. The precipitate was collected via suction filtration. The polymer was purified by Soxhlet extraction with hexane for 20h, followed by acetone for 20h and finally washed down by chloroform. The chloroform part was concentrated and dropped into methanol solution with rigorous stirring. The precipitate was collected via suction filtration, thoroughly washed with methanol and dried under vacuum. (210mg, 68%)

Polymer 12:



- To a dry round bottom flask was added 1,4-bis(5-bromofuran-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (216mg, 0.3mmol), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (232 mg, 0.3mmol), $\text{Pd}_2(\text{dba})_3$ (3 mol%, 0.009mmol, 8.5mg), $\text{P}(\text{o-tol})_3$ (12 mol%, 0.036mmol, 11 mg) and toluene (10ml). The mixture was purged with argon for 30 min and then heated to 100°C for 16h. After cooling to room temperature, chloroform was added to dilute the solution and then extraction with water was done for three times.
- The organic layer was collected and dried by rotary evaporation. The residue was dissolved in minimal amount of chloroform and precipitated into methanol solution. The precipitate was collected via suction filtration. The polymer was purified by Soxhlet extraction with hexane for 20h, followed by acetone for 20h and finally washed down by chloroform. The chloroform part was concentrated and dropped into methanol solution with rigorous stirring. The precipitate was collected via suction filtration, thoroughly washed with methanol and dried under vacuum. (200mg, 67%)

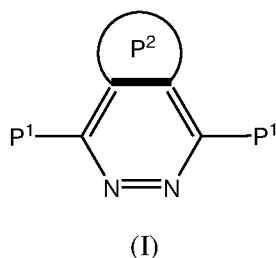
Industrial Applicability

The compounds of Formula (VI), (VIIa) and (VIIb) as defined above may be useful in the manufacture of the compounds of Formula (I). The compound of Formula (I) may be useful in the manufacture of the compounds of Formula (IV). The compounds of Formula (IV) may be
5 useful in the manufacture of semiconductor devices. The semiconductor devices manufactured using the compound of Formula (IV) as defined above may be used in a wide range of applications such as electrochromic materials, organic light-emitting diode, organic thin-film transistors and organic photovoltaic cells. As the NIR absorption properties can be reversibly
10 switched by applying/removing a low voltage on the thin film, the materials may have applications in smart glass or smart window applications.

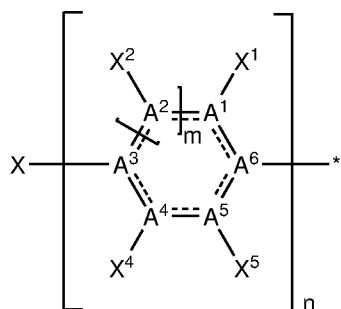
It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

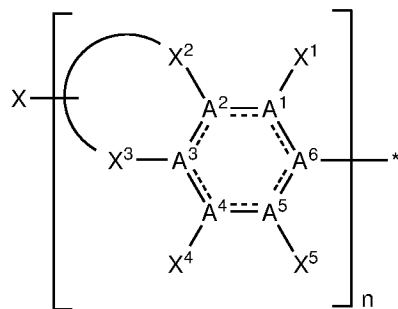
1. A compound having the following Formula (III);



- 5 wherein P¹ has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

wherein

----- is a single or double bond, as valency allows;

- 10 m is 0 or 1;

n is an integer selected from 1 to 4;

X, X¹, X², X³, X⁴ and X⁵ are independently absent or selected from the group consisting of a bond, H, halogen, CN, R¹, OR¹ or SR¹;

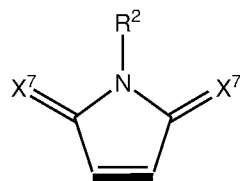
- 15 wherein R¹ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A¹ is selected from the group consisting of O, S, Se, Te, C and N

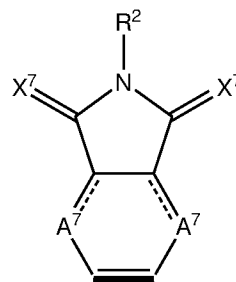
A², A³, A⁴, A⁵ and A⁶ are independently C or N; and

- 20 wherein any two substituents selected from the group consisting of X¹, X², X³, X⁴ and X⁵ may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

- 25 and wherein P² has the following formula (IIIa) or (IIIb);



(IIIa)



(IIIb)

wherein

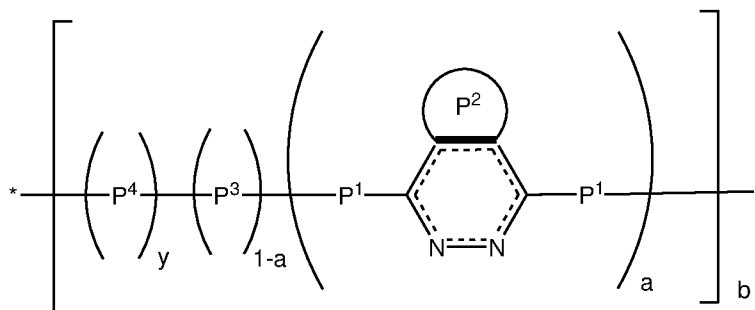
R² is an optionally substituted alkyl or optionally substituted aryl;

5 X⁷ is O or S;

A⁷ is CH, CH₂ or N;

and  is where the compound of Formula (IVa) or (IVb) is fused to the compound of Formula (I).

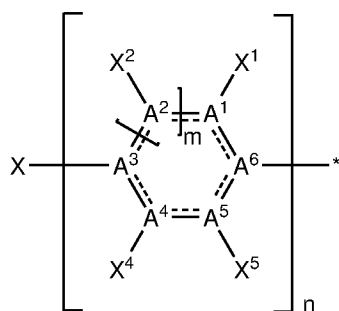
2. A compound having repeating units of the following Formula (III);



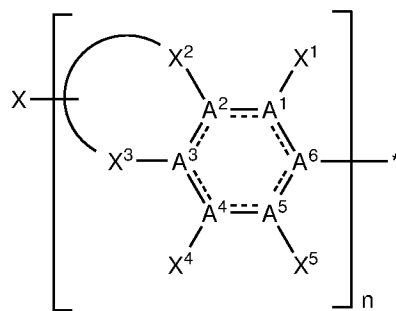
10

(IV)

wherein P¹ has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

15

wherein

 is a single or double bond, as valency allows;

m is 0 or 1;

n is an integer selected from 1 to 4;

X^1 , X^2 , X^3 , X^4 and X^5 are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^1 , OR^1 or SR^1 ;

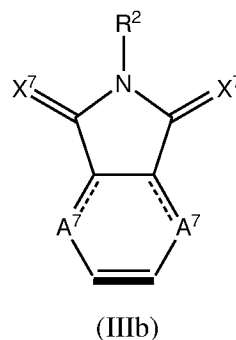
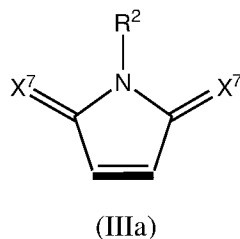
wherein R^1 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A^1 is selected from the group consisting of O, S, Se, Te, C and N

A^2 , A^3 , A^4 , A^5 and A^6 are independently C or N; and

wherein any two substituents selected from the group consisting of X^1 , X^2 , X^3 , X^4 and X^5 may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.;

P^2 has the following formula (IIIa) or (IIIb);



wherein

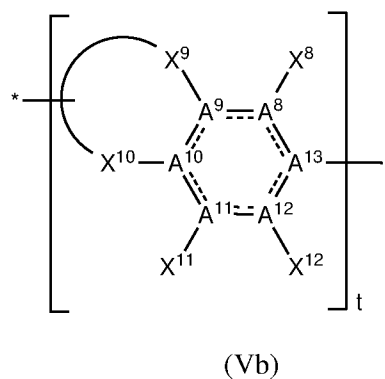
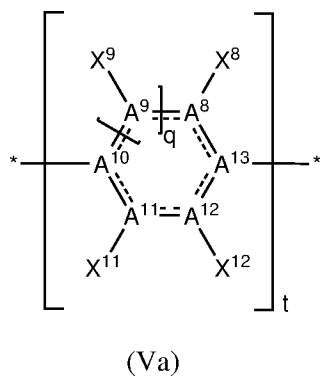
R^2 is an optionally substituted alkyl or optionally substituted aryl;

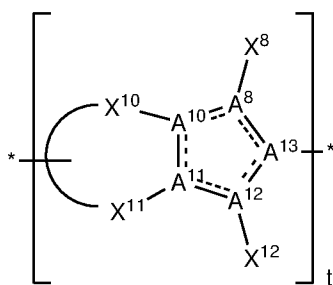
X^7 is O or S;

A^7 is CH, CH_2 or N;

and is where the compound of Formula (IIIa) or (IIIb) is fused to the compound of Formula (IV);

P^3 has the following Formula (Va), (Vb) or (Vc) ;





(Vc)

wherein

q is 0 or 1;

5 t is an integer selected from 1 to 4;

X^8 , X^9 , X^{11} and X^{12} are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^3 , OR^3 or SR^3 ;

10 wherein R^3 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

A^8 is selected from the group consisting of O, S, Se, Te, C and N

A^9 , A^{10} , A^{11} , A^{12} and A^{13} are independently C or N;

15 wherein any two substituents selected from the group consisting of X^8 , X^9 , X^{10} , X^{11} and X^{12} may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

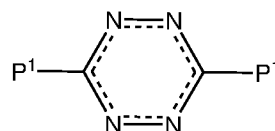
20 and P^4 is absent, or is an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

a is any value from 0 to 1; and

b is an integer selected from 1 to 10,000; and

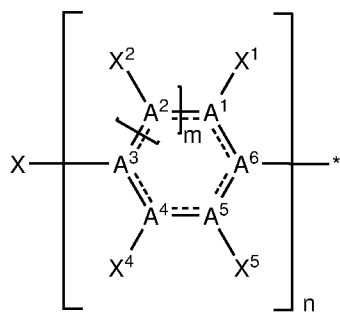
25 y is an integer selected from 0 to 5.

3. A compound having the following Formula (I);

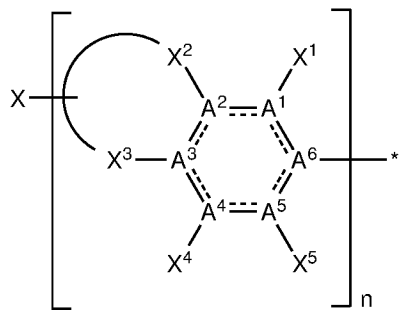


(VI)

wherein P^1 has the following Formula (IIa) or (IIb);



(IIa)



(IIb)

wherein

==== is a single or double bond, as valency allows;

5 m is 0 or 1;

n is an integer selected from 1 to 4;

X, X¹, X², X³, X⁴ and X⁵ are independently absent or selected from the group consisting of a bond, H, halogen, CN, R¹, OR¹ or SR¹;

wherein R¹ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl;

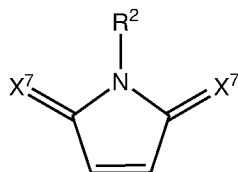
A¹ is selected from the group consisting of O, S, Se, Te, C and N;

A^2, A^3, A^4, A^5 and A^6 are independently C or N; and

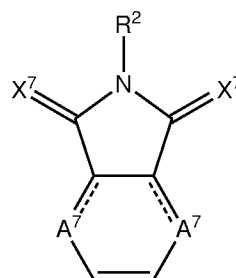
15 wherein any two substituents selected from the group consisting of X¹, X², X³, X⁴ and X⁵ may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl.

20

4. A compound having the following formula (VIIa) or (VIIb);



(VIIa)



(VIIb)

wherein

25 ----- is a single or double bond, as valency allows;

R^2 is an optionally substituted alkyl or optionally substituted aryl;

X^7 is O or S; and

A^7 is CH, CH_2 or N.

5 5. The compound according to any one of claims 1 to 3, wherein halogen is selected from the group consisting of F, Cl, Br and I.

6. The compound according to any one of claims 1 to 3, wherein the optionally substituted alkyl is an optionally substituted C_1 - C_{25} alkyl, the optionally substituted alkenyl is an optionally substituted C_2 - C_{25} alkenyl, the optionally substituted alkynyl is an optionally substituted C_2 - C_{25} alkynyl, the optionally substituted cycloalkyl is an optionally substituted C_3 - C_{12} cycloalkyl, the optionally substituted heterocycloalkyl is an optionally substituted C_3 - C_{12} heterocycloalkyl, the optionally substituted cycloalkenyl is an optionally substituted C_3 - C_{12} cycloalkenyl, the optionally substituted heterocycloalkenyl is an optionally substituted C_3 - C_{12} heterocycloalkenyl, the optionally substituted aryl is an optionally substituted C_3 - C_{18} aryl and the optionally substituted heteroaryl is an optionally substituted C_3 - C_{18} heteroaryl.

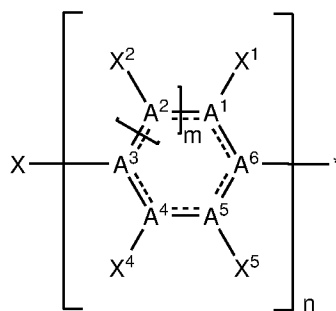
15 7. The compound according to claim 6, wherein the optionally substituted heterocycloalkyl and optionally substituted heteroaryl are independently a 3- to 18-membered monocyclic, bicyclic, or polycyclic ring.

8. The compound of claim 7, wherein X is selected from the group consisting of halogen, CN, R^1 and OR^1 .

20 9. The compound according to claim 8, wherein R^1 is optionally substituted alkyl.

10. The compound according to any one of claims 1 to 3, wherein P^1 is selected from the group consisting of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted tellurophene, optionally substituted pyrrole, optionally substituted phenylene, optionally substituted aza-phenylene, optionally substituted arylene diimide, optionally substituted fluorene, optionally substituted cabazole, optionally substituted dibenzodioxole, optionally substituted benzoxodiazole, optionally substituted benzotriazole, optionally substituted benzothiadiazole and any combination thereof.

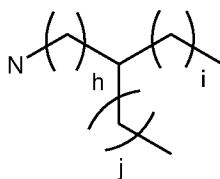
11. The compound according to any one of claims 1 to 3, wherein P^1 has the following Formula (IIa);



(IIa).

12. The compound according to claim 11, wherein m is 0.

13. The compound according to claim 12, wherein A¹ is N.
14. The compound according to claim 13, wherein X¹ is H.
15. The compound according to claim 12, wherein A³, A⁴, A⁵ and A⁶ are C.
16. The compound according to claim 15, wherein X⁴ and X⁵ are independently selected from the group consisting of H, R¹ and OR¹.
17. The compound according to claim 16, wherein R¹ is optionally substituted alkyl.
18. The compound according to claim 12, wherein A¹ is S; X¹ is absent; A³, A⁴, A⁵ and A⁶ are C, X⁴ and X⁵ are H and X is Br.
19. The compound according to claim 12, wherein A¹ is O; X¹ is absent; A³, A⁴, A⁵ and A⁶ are C, X⁴ and X⁵ are H and X is Br.
20. The compound according to claim 11, wherein m is 1.
21. The compound according to claim 20, wherein A³ and A⁶ are C.
22. The compound according to claim 21, wherein X¹, X², X⁴ and X⁶ are independently absent or selected from the group consisting of H, halogen, R¹ and OR¹.
23. The compound according to claim 22, wherein R¹ is optionally substituted alkyl.
24. The compound of claim 20, wherein A¹, A², A³, A⁴, A⁵ and A⁶ are C.
25. The compound according to claim 24, wherein X¹, X², X⁴ and X⁶ are independently H or halogen.
26. The compound according to any one of claims 1 or 2, wherein P² is selected from the group consisting of optionally substituted imide and optionally substituted phthalamide.
27. The compound according to any one of claims 1, 2 or 4, wherein R² is an optionally substituted alkyl.
28. The compound according to claim 27, wherein the optionally substituted alkyl is an optionally substituted linear alkyl or an optionally substituted branched alkyl.
29. The compound according to claim 28, wherein the optionally substituted linear alkyl is an optionally substituted C₁ to C₂₅ linear alkyl.
30. The compound according to claim 28, wherein the optionally substituted branched alkyl is an optionally substituted C₁ to C₂₅ branched alkyl.
31. The compound according to claim 30, wherein the optionally substituted branched alkyl has the following formula (XII).



(XII)

wherein

h is 0 or 1; and

i and j are independently integers selected from 1 to 13.

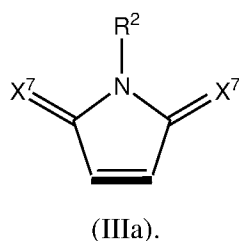
32. The compound according to claim 31, wherein h is 1.

5 33. The compound according to claim 32, wherein i is 7; and j is 9.

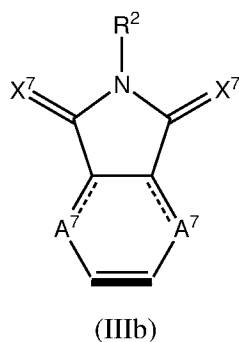
34. The compound according to claim 33, wherein the optionally substituted alkyl is 2-octyldodecyl.

35. The compound according to any one of claims 1, 2 or 4, wherein X^7 is O.

10 36. The compound according to any one of claims 2 or 4, wherein P^2 has the following formula (IIIa):

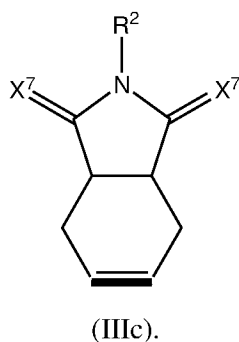


37. The compound according to any one of claims 2 or 4, wherein P^2 has the following formula (IIIb):



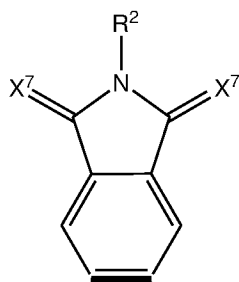
38. The compound according to claim 37, wherein A^7 is CH_2 .

39. The compound according to claim 38, wherein P^2 has the following Formula (IIIc):



40. The compound according to claim 38, wherein A^7 is CH.

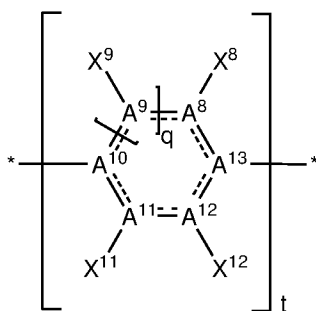
41. The compound according to claim 40, wherein P^2 has the following Formula (IIIId):



(IIIId).

42. The compound according to claim 2, wherein P^3 is selected from the group consisting of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted pyrrole, optionally substituted phenyl, optionally substituted fluorenes, optionally substituted carbazoles, optionally substituted fused furans and optionally substituted fused thiophenes.

43. The compound according to claim 2, wherein P^3 has the following formula (Va);



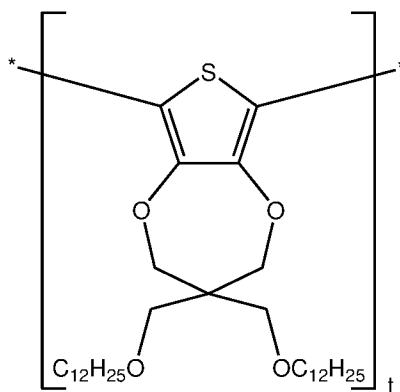
(Va).

44. The compound according to claim 43, wherein q is 0.

45. The compound according to claim 44, wherein A^8 is N.

The compound according to claim 45, wherein X^8 is H.

46. The compound according to claim 44, wherein A^8 is S; X^8 is absent; and A^{10} , A^{11} , A^{12} and A^{13} are C.
47. The compound according to claim 46, wherein X^{11} and X^{12} are taken together to form an optionally substituted 7-membered heterocycloalkyl.
48. The compound according to claim 47, wherein P^3 has the following Formula (XVI);



(XVI).

49. The compound according to claim 43, wherein q is 1.

50. The compound according to claim 49, wherein A^{10} and A^{13} are C.

51. The compound according to claim 50, wherein X^8 , X^9 , X^{11} and X^{12} are independently selected from the group consisting of H, halogen, R^3 and OR^3 .

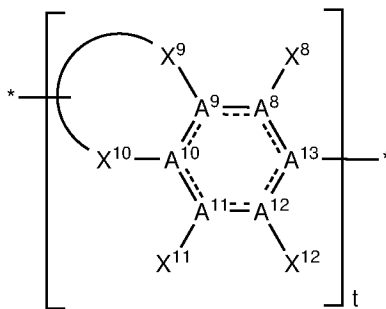
52. The compound according to claim 51, wherein R^3 is optionally substituted alkyl.

53. The compound of claim 52, wherein A^8 , A^9 , A^{10} , A^{11} , A^{12} and A^{13} are C.

54. The compound according to claim 53, wherein X^8 , X^9 , X^{11} and X^{12} are independently selected from the group consisting of H, halogen, OR^{10} and SR^{10} .

55. The compound according to claim 54, wherein R^{10} is an optionally substituted alkyl.

56. The compound according to claim 2, wherein P^3 has the following formula (Vb);



(Vb).

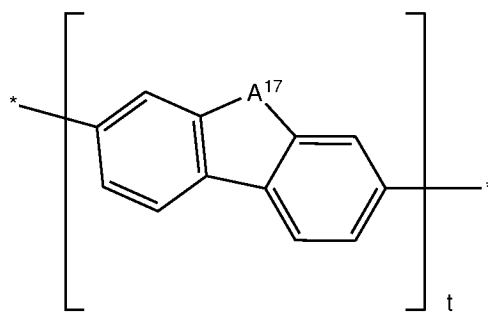
57. The compound according to claim 56, wherein A^8 , A^9 , A^{10} , A^{11} , A^{12} and A^{13} are C.

58. The compound according to claim 57, wherein X^8 , X^{11} and X^{12} are H.

59. The compound according to claim 58, wherein X^9 and X^{10} are taken together to form an optionally substituted 5-membered heterocycloalkyl.

60. The compound according to claim 59, wherein the optionally substituted 5-membered heterocycloalkyl is further fused with an optionally substituted 6-membered aryl.

61. The compound according to claim 60, wherein P^3 has the following formula (XVII);

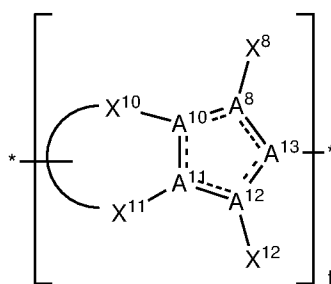


(XVII)

wherein A^{17} is selected from the group consisting of NH , CHR^{11} , $C(R^{11})_2$, $SiHR^{11}$ and $Si(R^{11})_2$; wherein R^{11} is optionally substituted alkyl.

62. The compound according to claim 61, wherein R^{11} is C_8H_{17} or $C_{12}H_{25}$.

63. The compound according to claim 2, wherein P^3 has the following Formula (Vc);



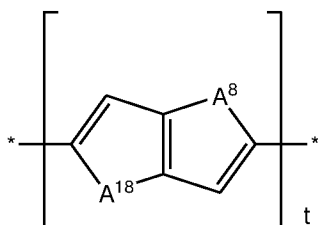
(Vc).

64. The compound according to claim 63, wherein A^{10} , A^{11} , A^{12} and A^{13} are C.

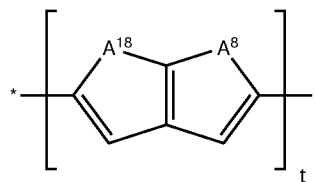
65. The compound according to claim 64, wherein X^8 and X^{12} are H.

66. The compound according to claim 65, wherein X^{10} and X^{11} are taken together to form an optionally substituted 5-membered heteroaryl.

67. The compound according to claim 66, wherein P^3 has the following Formula (XVIIIa) or (XVIIIb);



(XVIIIa)



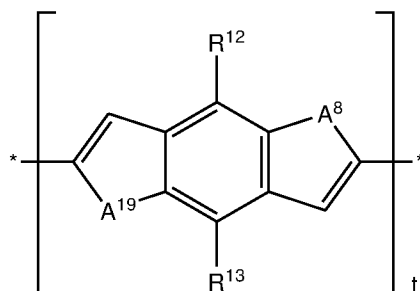
(XVIIIb)

wherein A^8 and A^{18} are independently selected from the group consisting of O, S and Se.

68. The compound according to claim 67, wherein X^{10} and X^{11} are taken together to form an optionally substituted 6-membered aryl.

69. The compound according to claim 68 wherein the optionally substituted 6-membered aryl is further fused with an optionally substituted 5-membered heteroaryl.

70. The compound according to claim 63, wherein P^3 has the following Formula (XIX);



(XIX)

wherein A^8 and A^{19} are independently selected from the group consisting of O, Se and S; and R^{12} and R^{13} are independently selected from R^{14} , OR^{14} , SR^{14} , wherein R^{14} is optionally substituted alkyl or optionally substituted aryl.

71. The compound according to claim 70, wherein R^{14} is an optionally substituted alkyl.

72. The compound according to claim 71, wherein R^{14} is C_8H_{17} .

73. The compound according to claim 71, wherein R^{14} is 2-ethylheptyl.

74. The compound according to claim 2, wherein a is 0.5, 0.3 or 0.1.

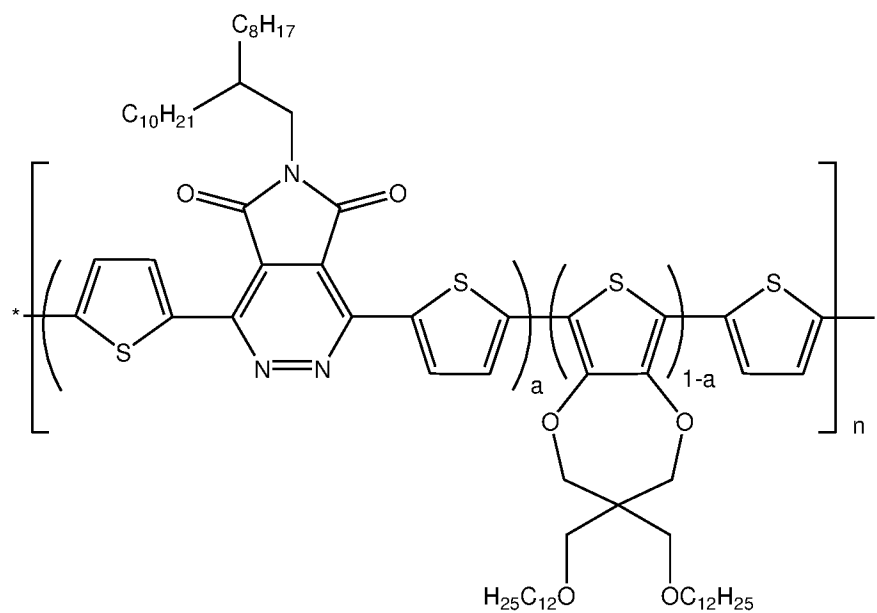
75. The compound according to claim 2, wherein b is an integer selected from 1 to 50.

76. The compound according to claim 2, wherein P^4 is selected from the group consisting of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted pyrrole, optionally substituted phenyl, optionally substituted fluorenes, optionally substituted carbazoles, optionally substituted fused furans and optionally substituted fused thiophenes.

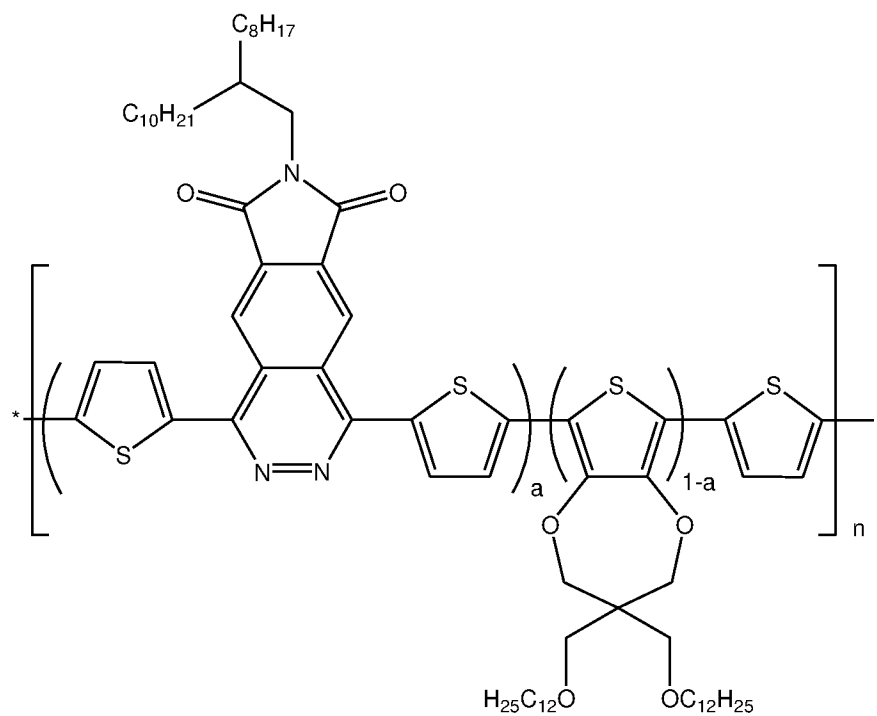
77. The compound according to claim 76, wherein P^4 is an optionally substituted thiophene or an optionally substituted fused thiophene.

78. The compound according to claim 2, wherein y is 1.

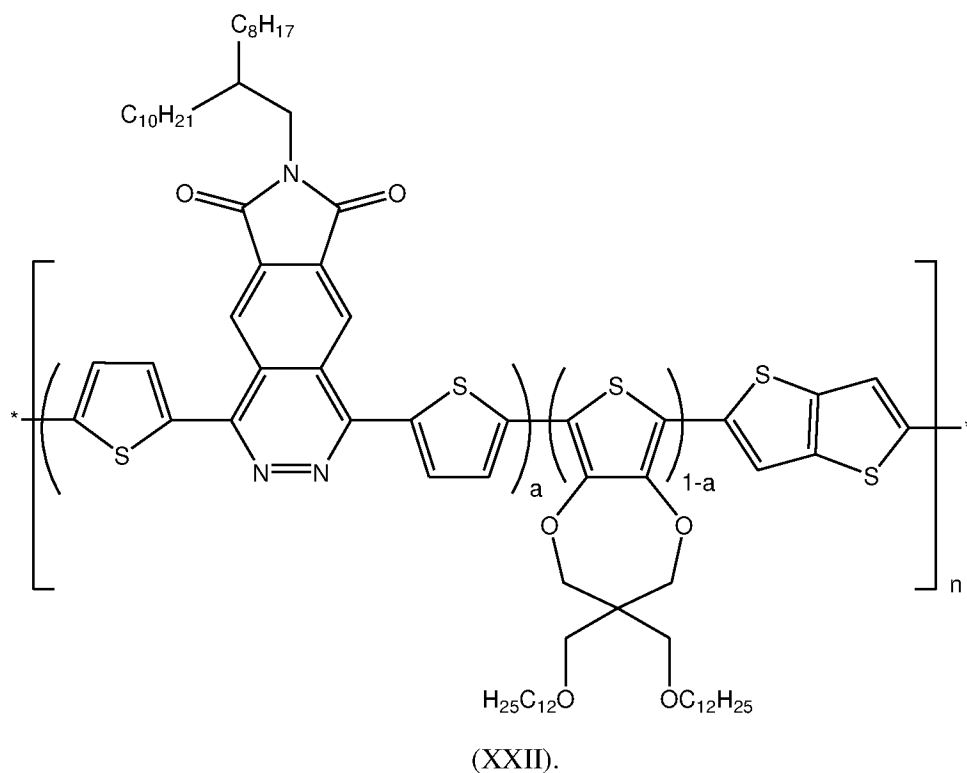
79. The compound according to claim 78, having the following formula (XX), (XXI), (XXII):



(XX).

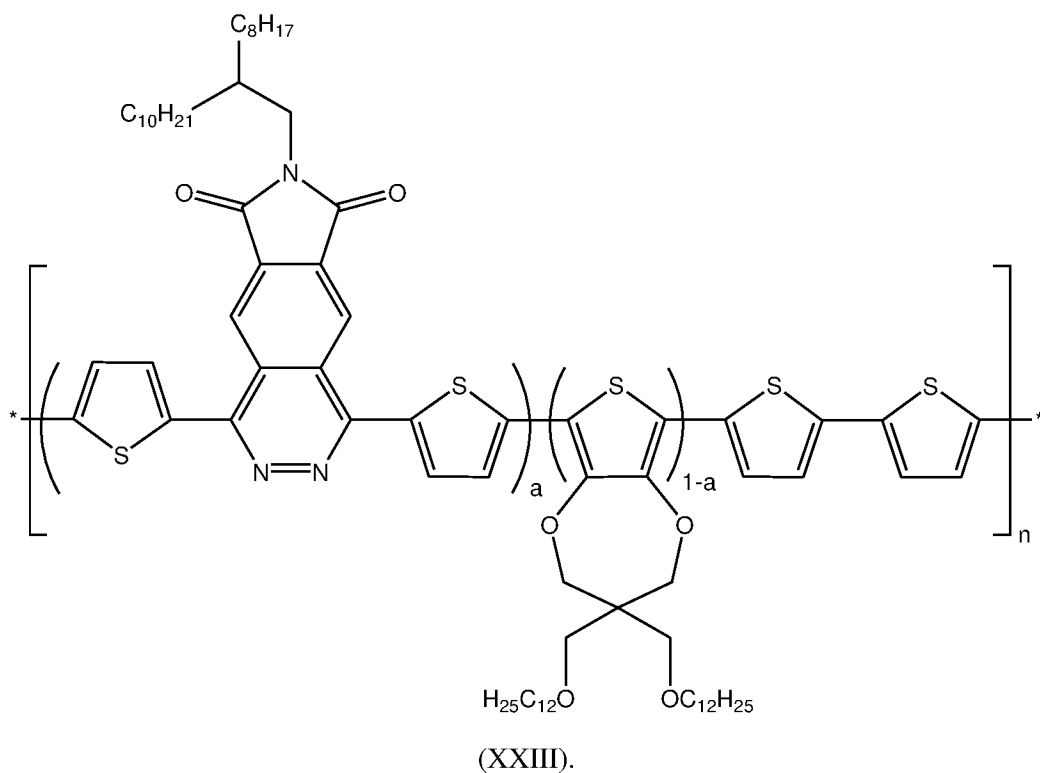


(XXI).

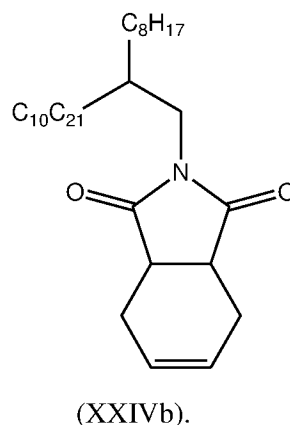
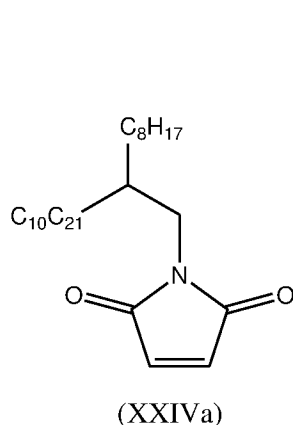


80. The compound according to claim 2, wherein y is 2.

81. The compound according to claim 80, having the following formula (XXIII),



82. The compound according to claim 4, having the following Formula (XXIVa) or (XXIVb),



83. A method for synthesizing the compound of Formula (VI) of claim 3, comprising the steps of providing a hydrazine and contacting the hydrazine with a functionalized cyclic group, wherein the cyclic group of the functionalized cyclic group is selected from the group comprising of optionally substituted furan, optionally substituted thiophene, optionally substituted selenophene, optionally substituted tellurophene, optionally substituted pyrrole, optionally substituted phenylene, optionally substituted aza-phenylene, optionally substituted arylene diimide, optionally substituted fluorene, optionally substituted cabazole, optionally substituted dibenzodioxole, optionally substituted benzooxodiazole, optionally substituted benzotriazole, optionally substituted benzothiadiazole and any combination thereof.

84. The method according to claim 83, wherein the functionalized cyclic group is functionalized with at least one nitrile group.

85. A method for synthesizing the compound of Formula (I) of claim 1, comprising the steps of:

providing the compound of Formula (VI) of claim 3; and

contacting the compound of Formula (VI) of claim 3 with the compound of Formulae (VIIa) or (VIIb) of claim 4 under reaction conditions to form the compound of Formula (I) of claim 1.

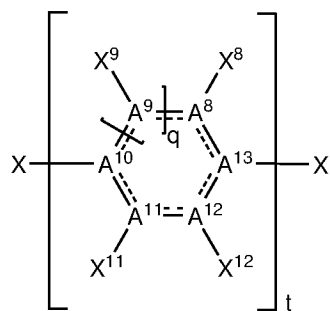
86. The method according to claim 85, further comprising the step of reacting the compound of claim 2 with N-bromosuccinimide and hydrogen peroxide, followed by a base.

87. A method for synthesizing the compound of Formula (IV) of claim 2, comprising the step of:

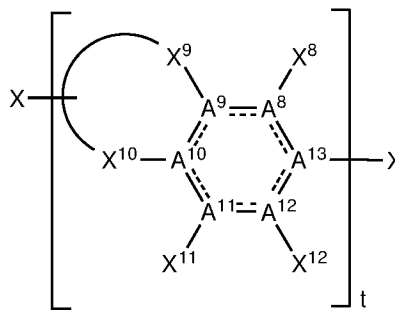
providing the compound of Formula (I) of claim 1; and

contacting the compound of Formula (I) of claim 1 with;

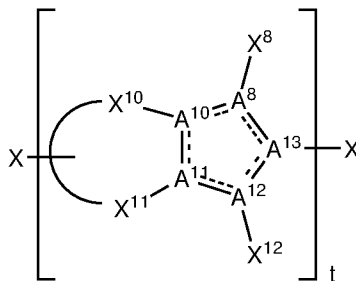
- (i) a compound having the following Formula (XXVa), (XXVb) or (XXVc) ;



(XXVa)



(XXVb)



(XXVc)

5

wherein

==== is a single or double bond, as valency allows;

q is 0 or 1;

t is an integer selected from 1 to 4;

10 X, X⁸, X⁹, X¹¹ and X¹² are independently absent or selected from the group consisting of a bond, H, halogen, CN, R³, OR³ or SR³;

wherein R³ is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

15

A⁸ is selected from the group consisting of O, S, Se, Te, C and N

A⁹, A¹⁰, A¹¹, A¹² and A¹³ are independently C or N; and

wherein any two substituents selected from the group consisting of X⁸, X⁹, X¹⁰, X¹¹ and X¹² may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl; and

20

(ii) a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group is selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

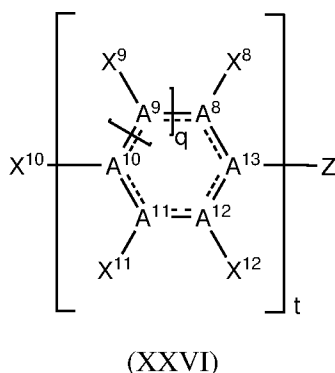
25

in the presence of a metal-containing catalyst.

88. A method for synthesizing the compound of Formula (IV) of claim 2, comprising the steps of:

1) providing the compound of Formula (I) of claim 1; and

5 2) contacting the compound of Formula (I) of claim 1 with a compound having the following Formula (XXVI);



wherein

10 --- is a single or double bond, as valency allows;

q is 0 or 1;

t is an integer selected from 1 to 4;

Z is a functional group containing zinc, tin or born;

15 X^8 , X^9 , X^{10} , X^{11} and X^{12} are independently absent or selected from the group consisting of a bond, H, halogen, CN, R^3 , OR^3 or SR^3 ;

wherein R^3 is selected from the group consisting of optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl, optionally substituted heteroaryl,

20 A^8 is selected from the group consisting of O, S, Se, Te, C and N

A^9 , A^{10} , A^{11} , A^{12} and A^{13} are independently C or N; and

25 wherein any two substituents selected from the group consisting of X^8 , X^9 , X^{10} , X^{11} and X^{12} may optionally be taken together to form an optionally substituted cyclic group selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

in the presence of a metal-containing catalyst to form a monomer precursor;

3) reacting the monomer precursor of step (2) with N-bromosuccinimide to form a reactive monomer; and

4) reacting the reactive monomer of step (2) with a cross-coupling reagent comprising a cyclic group; and an element selected from the group consisting of zinc, tin and boron; wherein the cyclic group is selected from the group consisting of an optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted cycloalkenyl, optionally substituted heterocycloalkenyl, optionally substituted aryl and optionally substituted heteroaryl;

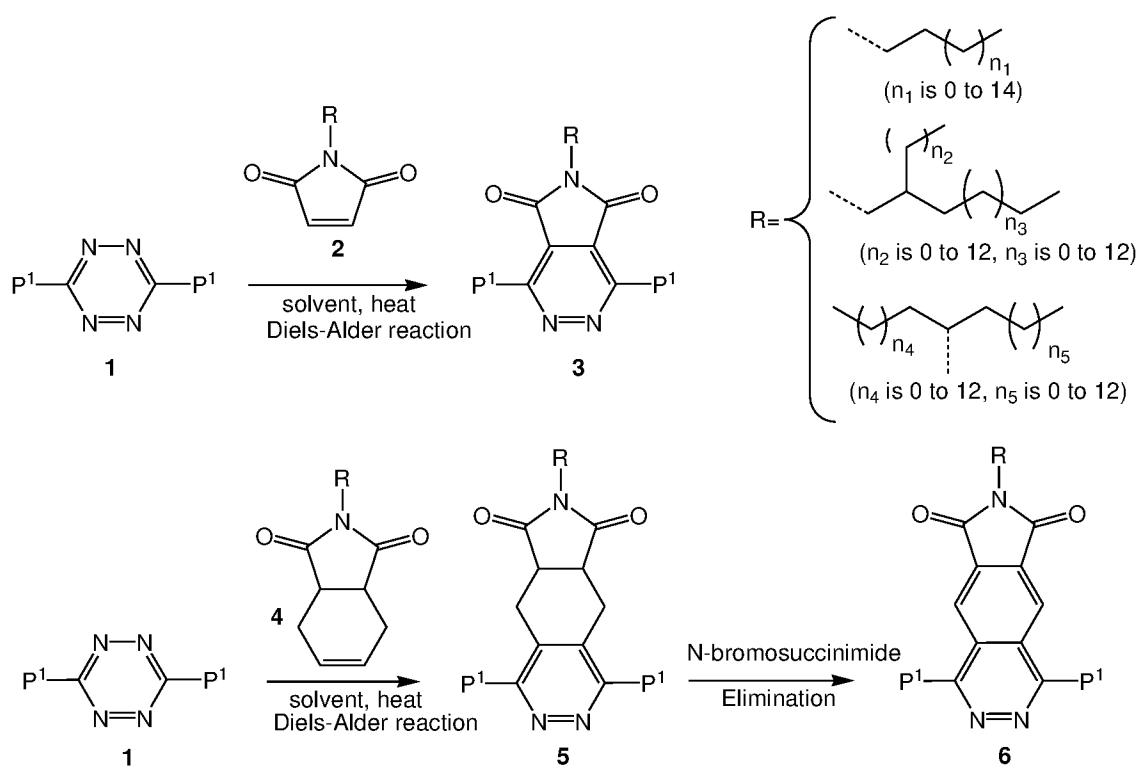
in the presence of a metal-containing catalyst.

89. The method of claim 78 or 88, wherein the metal in the metal-containing catalyst is selected from the group consisting of palladium, nickel and copper.

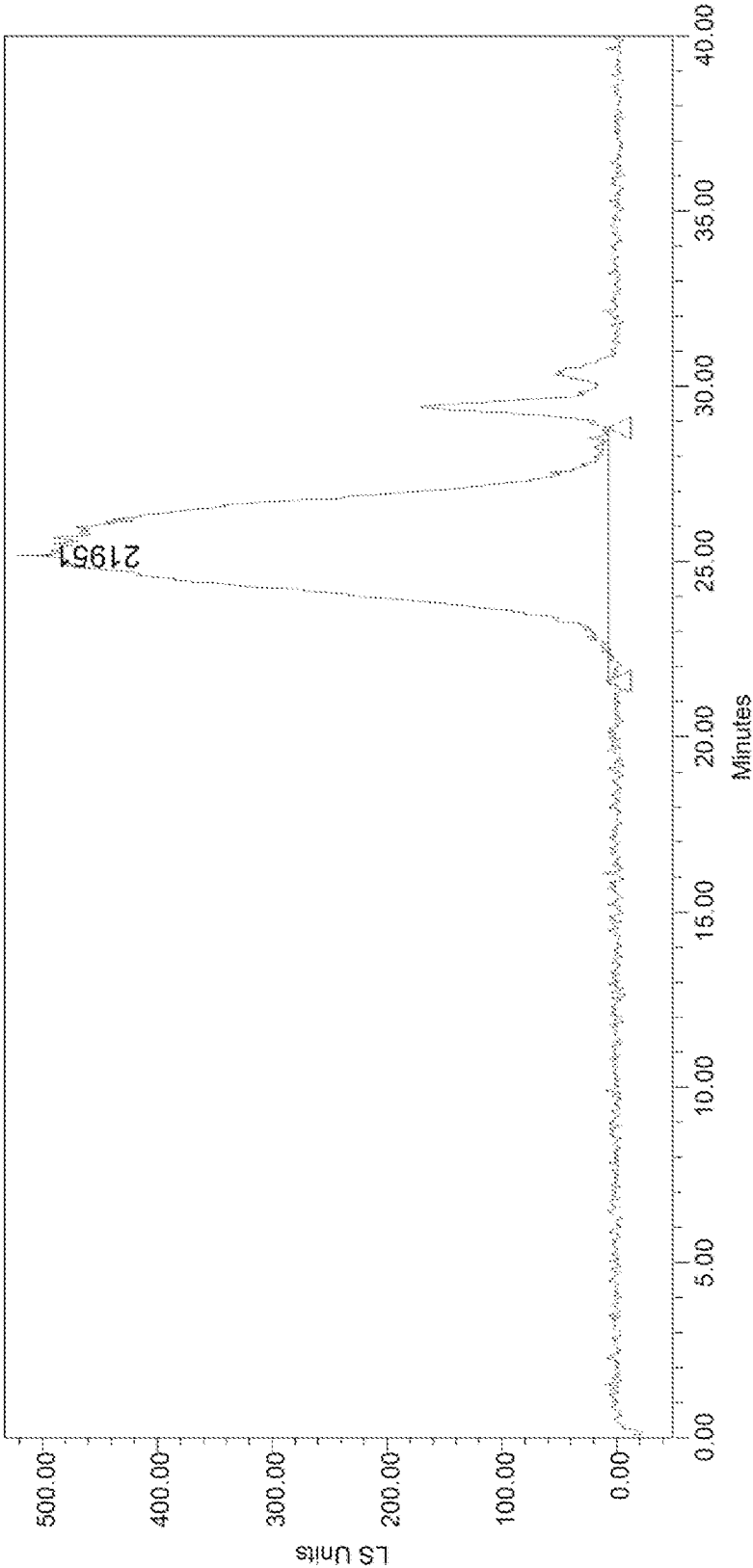
90. Use of the compound of Formula (V) of claim 2 in the manufacture of semiconductor devices.

91. A semiconductor device comprising the compound of Formula (V) of claim 2.

[Fig 1]



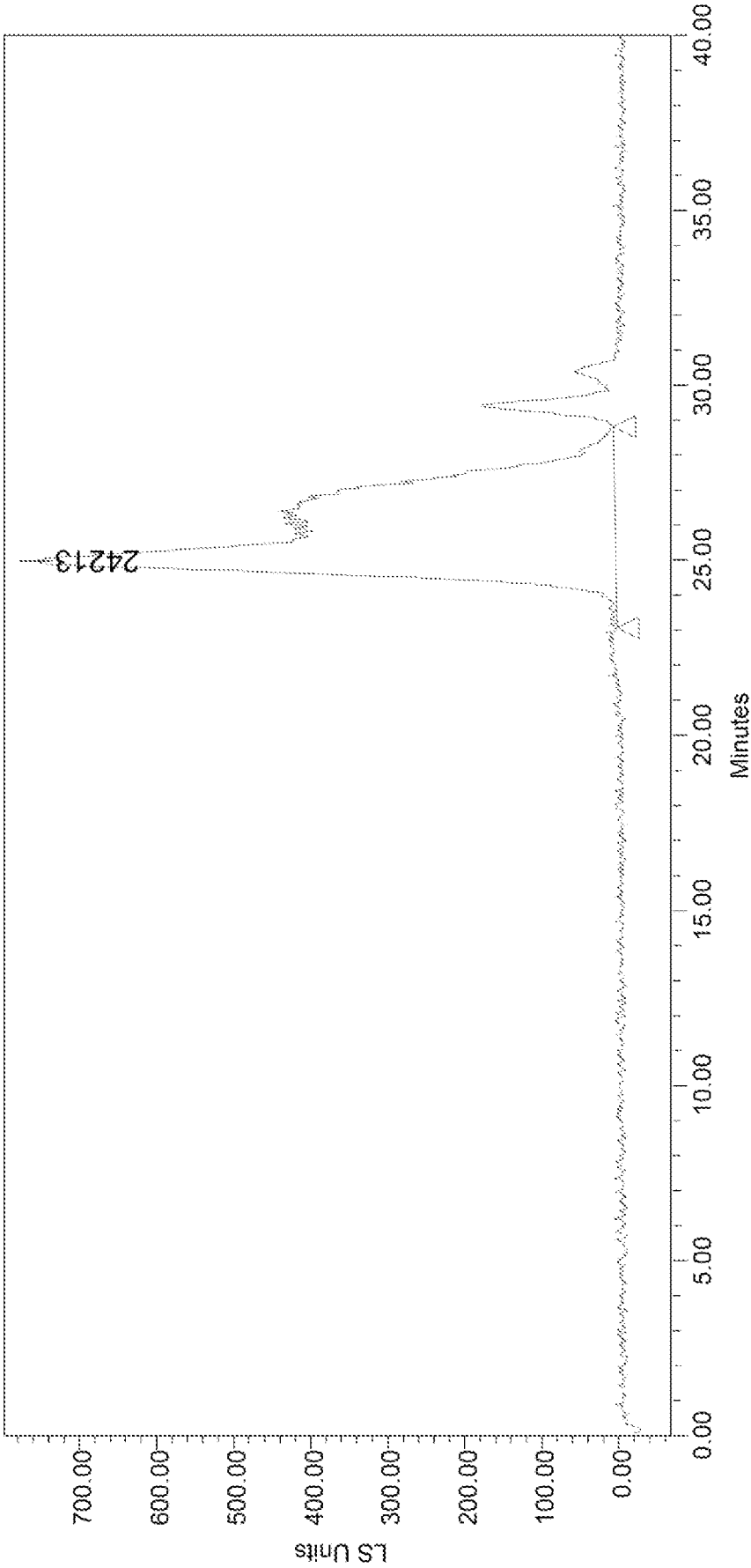
[Fig. 2]



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	16854	21838	21951	28223	35732		1.295729		

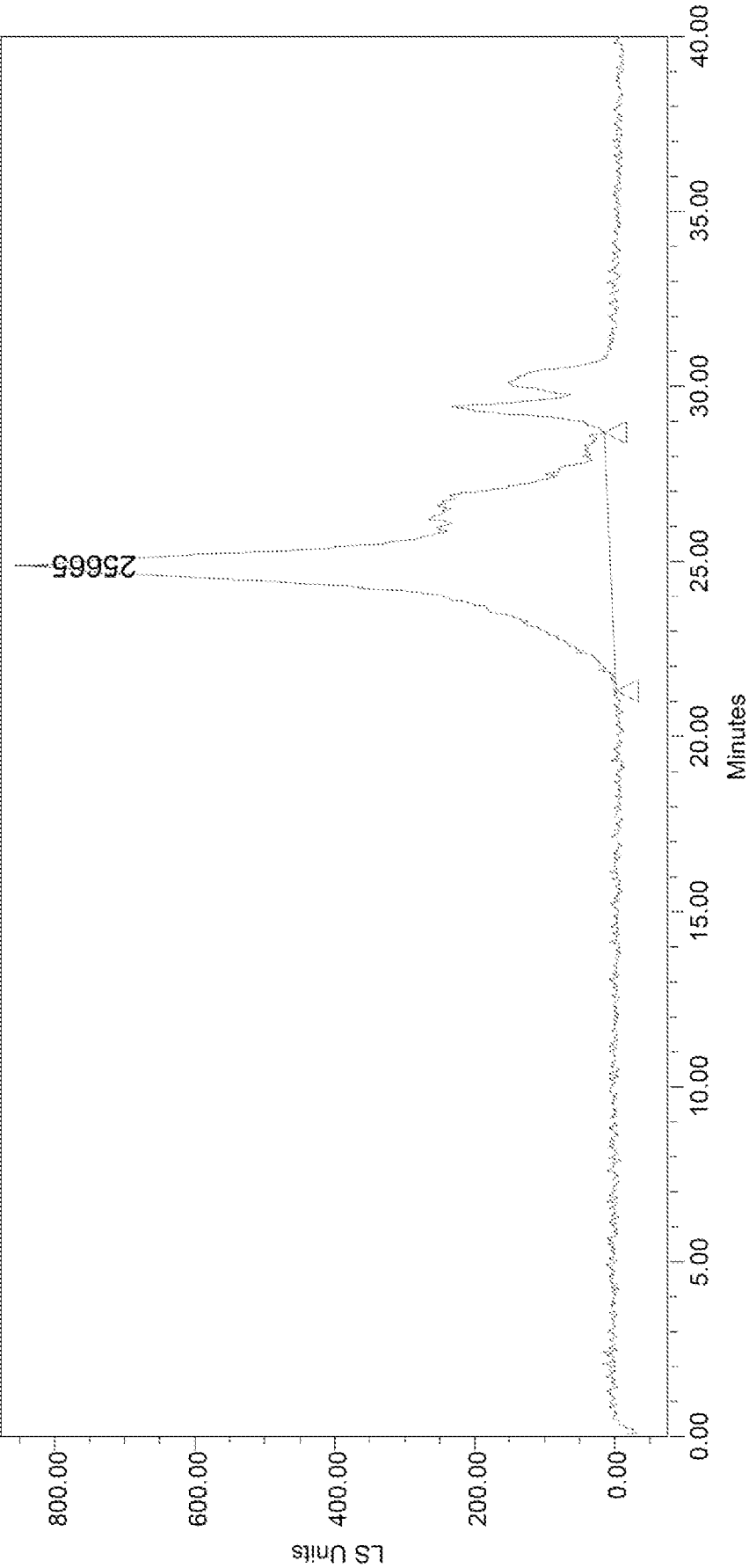
[Fig. 3]



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	13455	17246	24213	20858	23800		1.281774		

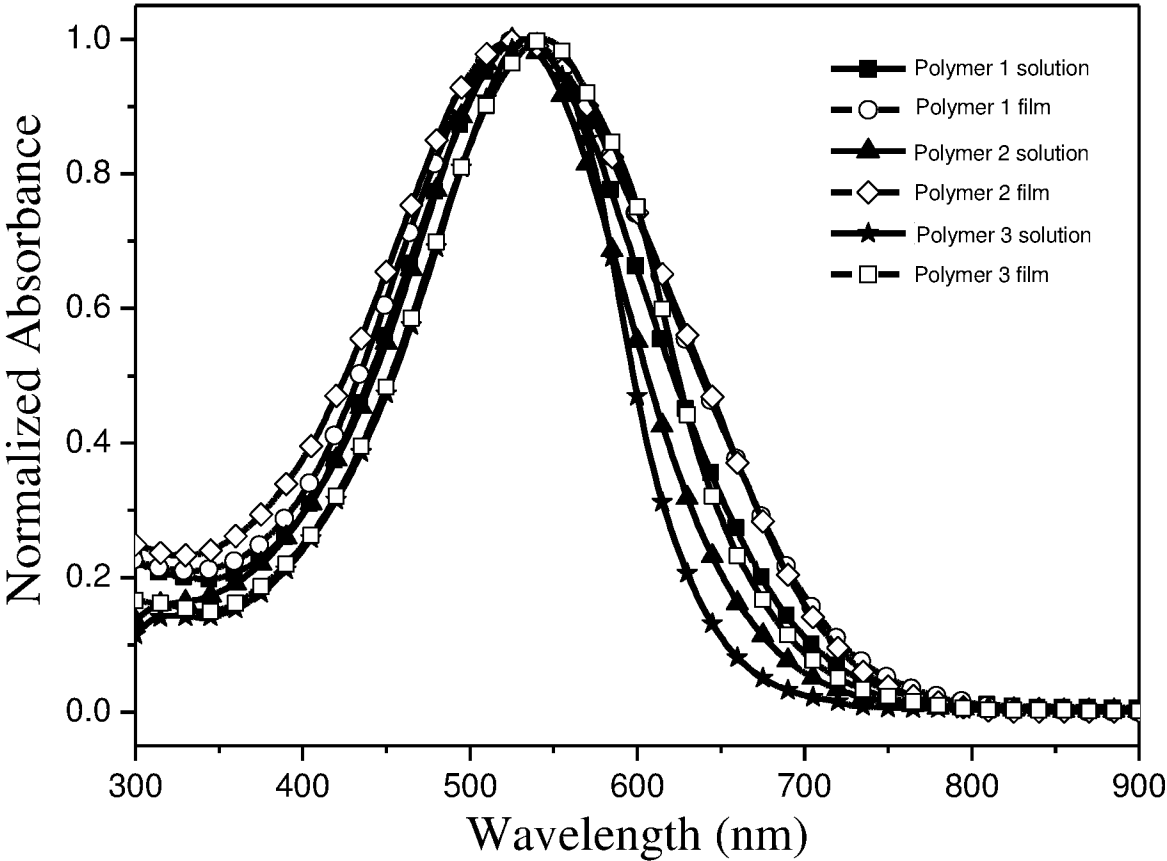
[Fig. 4]



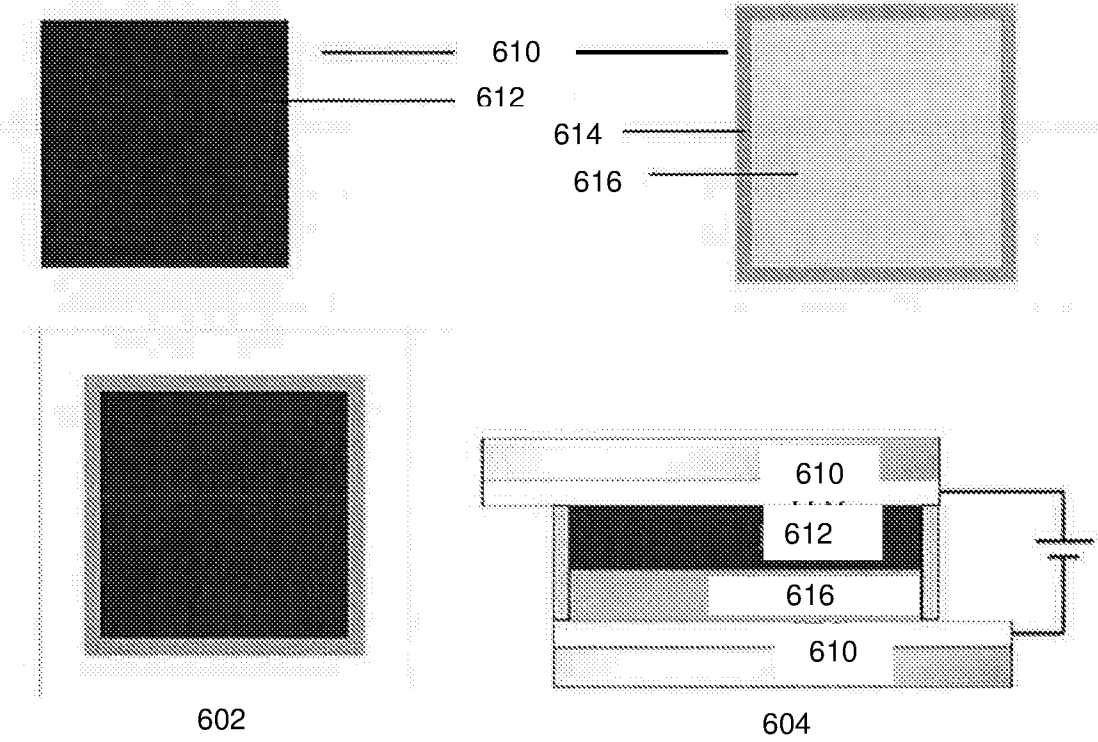
GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	18833	28177	25665	42667	64578		1.496120		

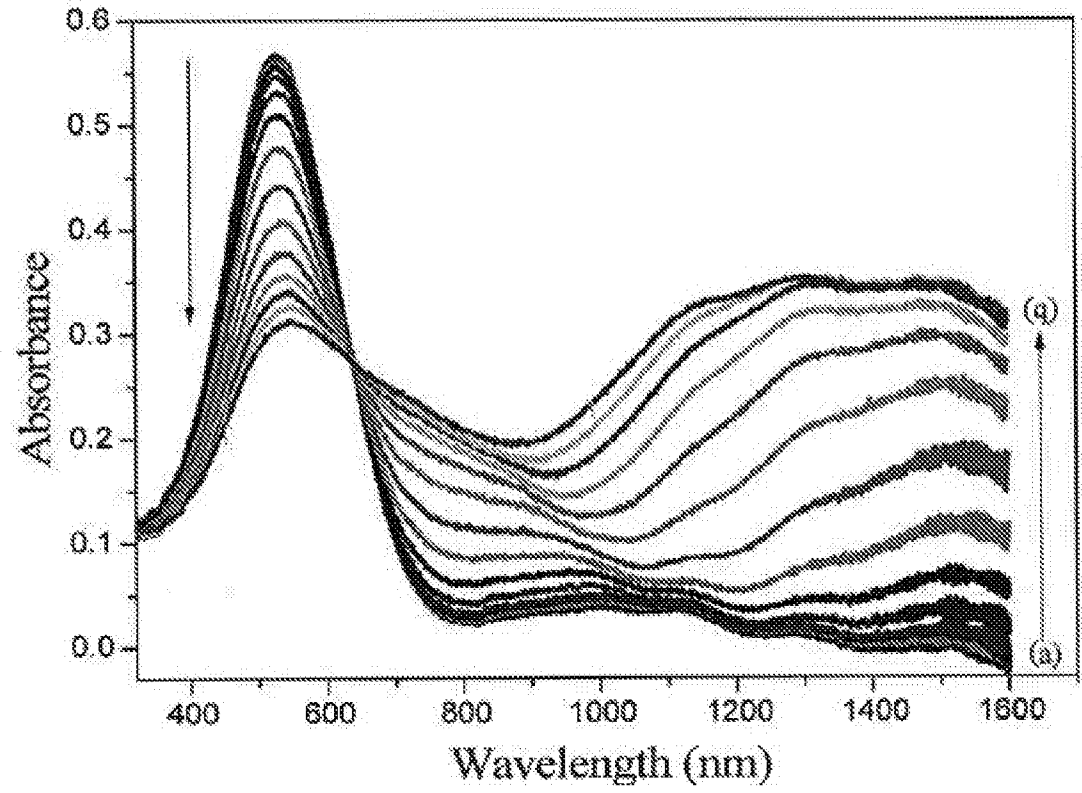
[Fig 5]



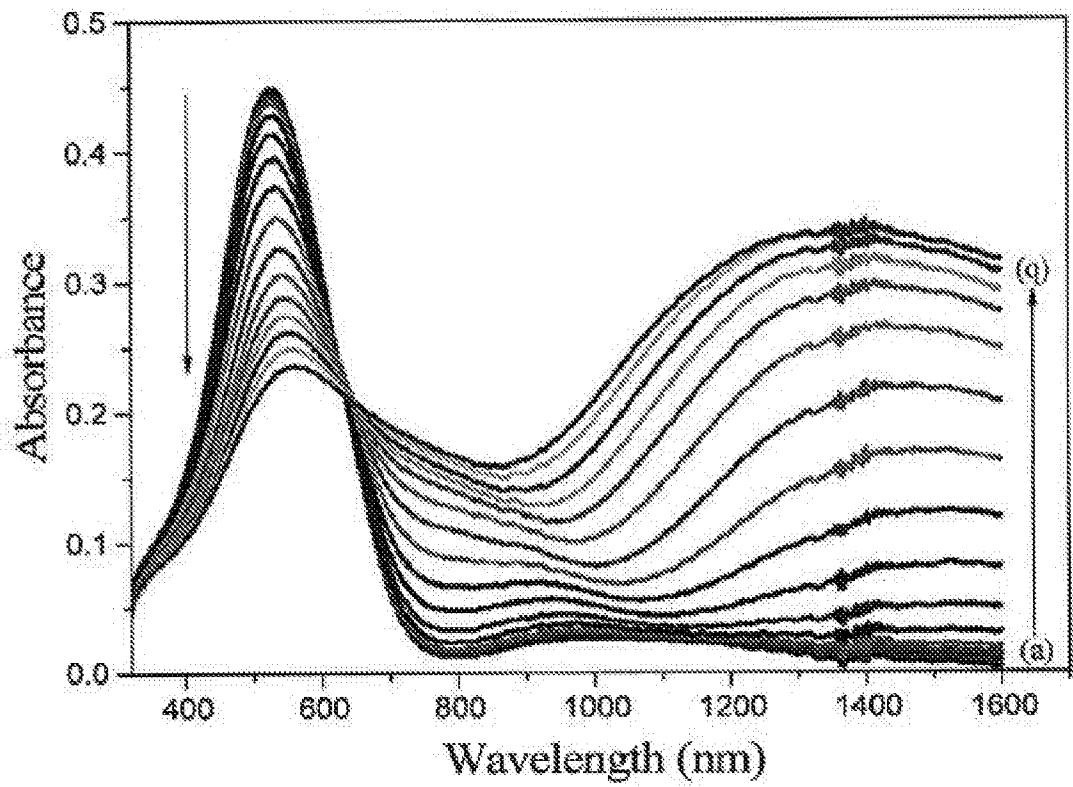
[Fig. 6]



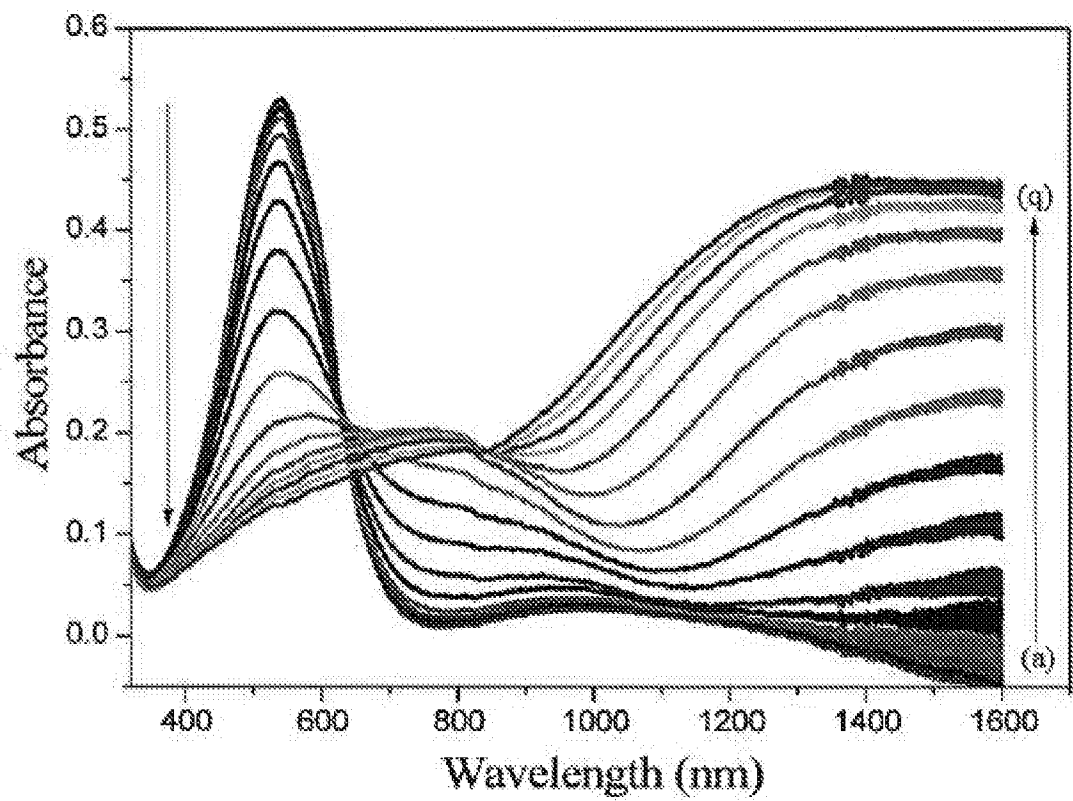
[Fig. 7]



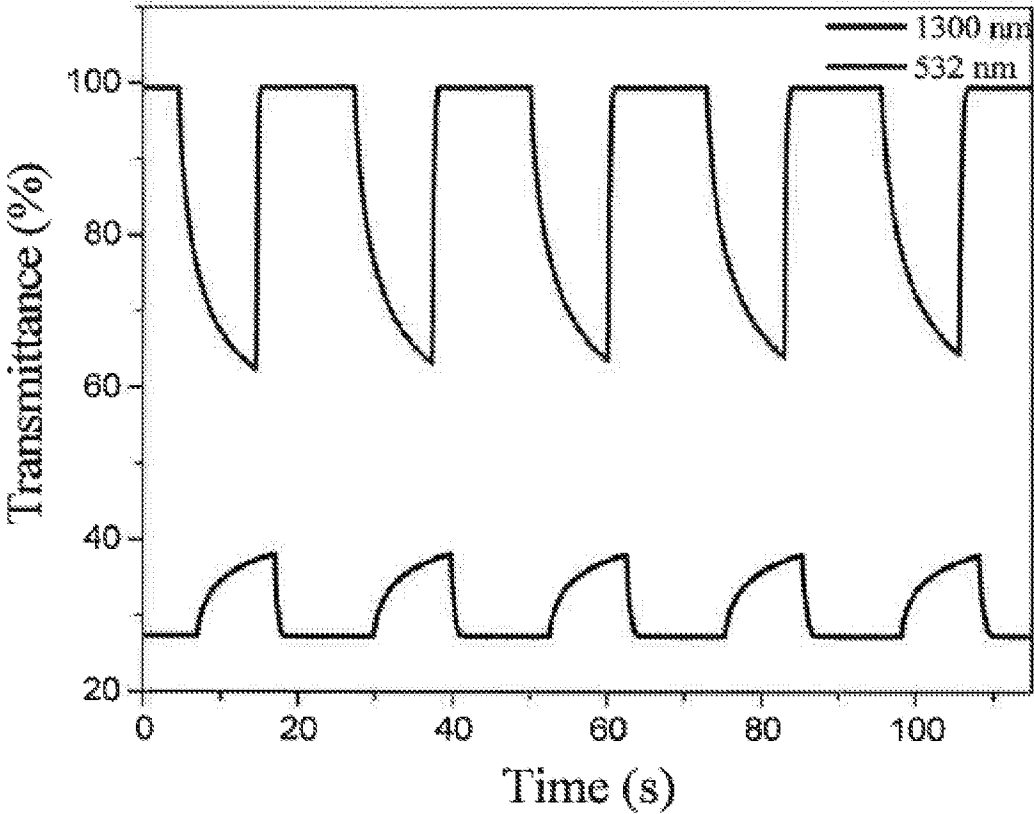
[Fig. 8]



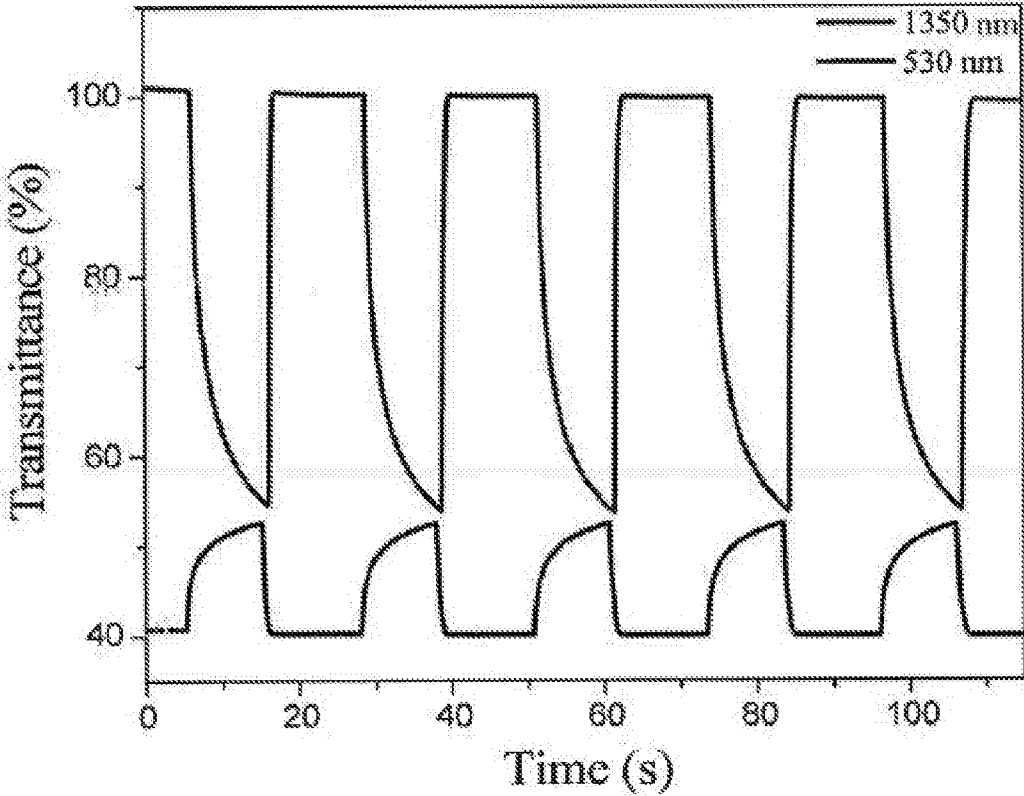
[Fig. 9]



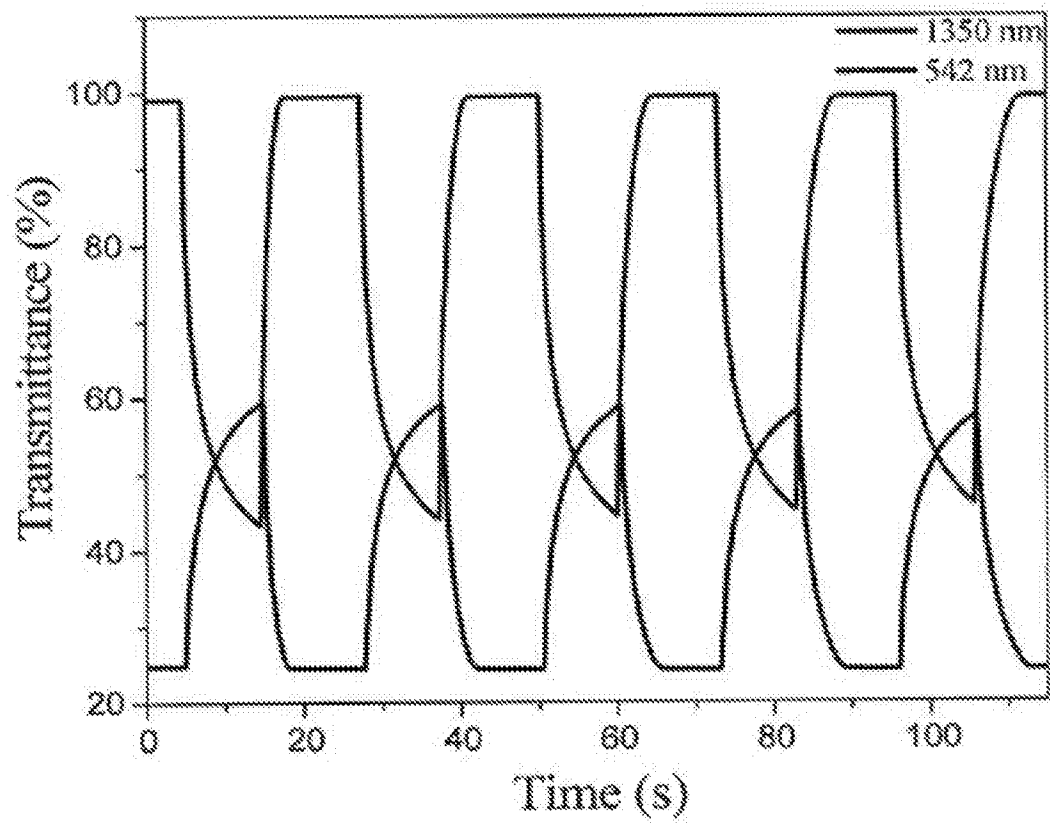
[Fig. 10]



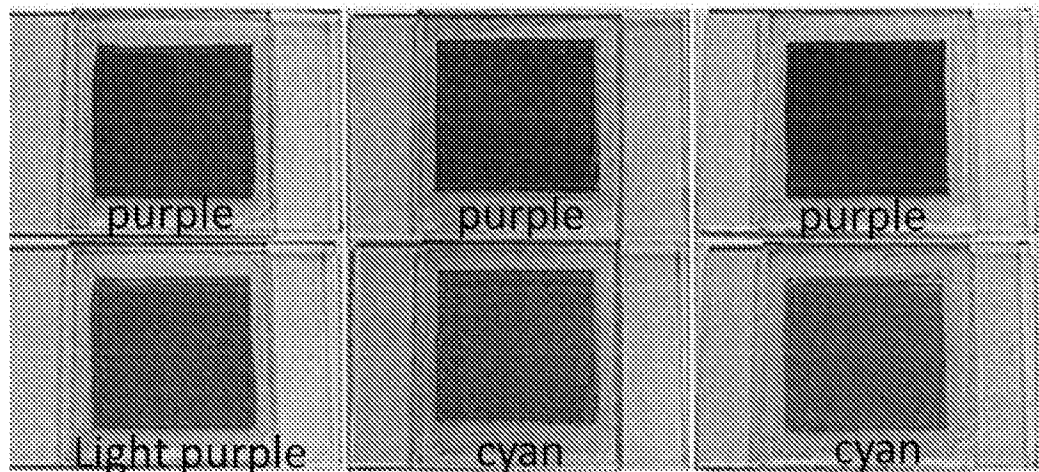
[Fig. 11]



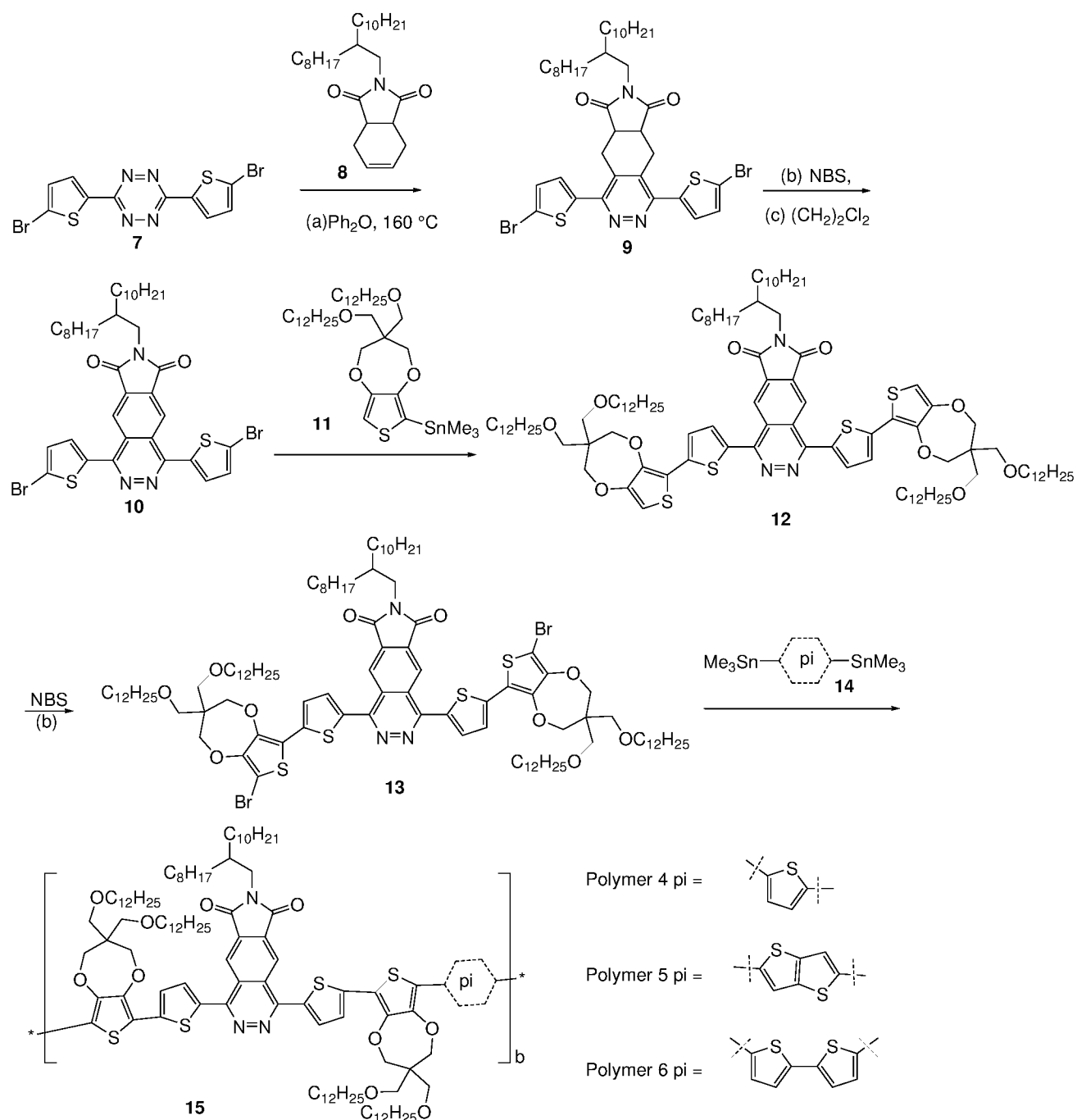
[Fig. 12]



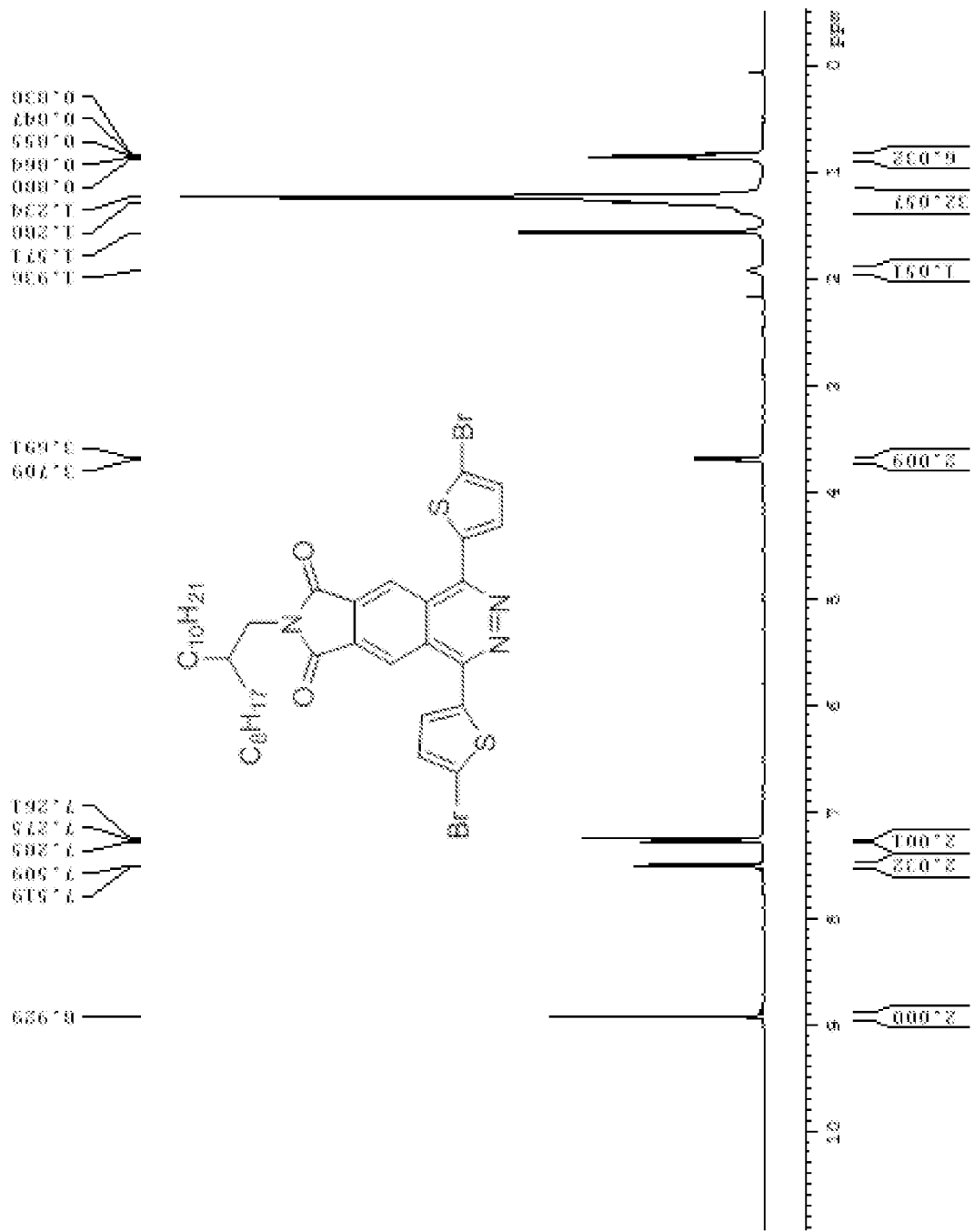
[Fig. 13]



[Fig. 14]

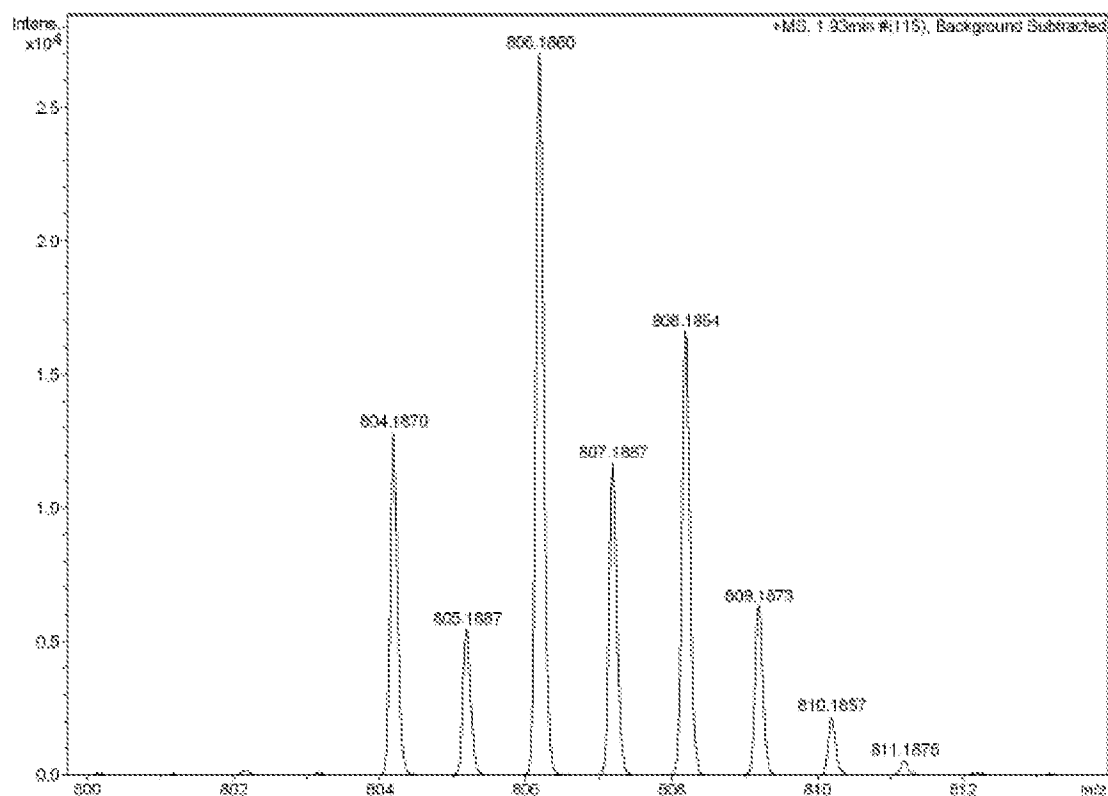


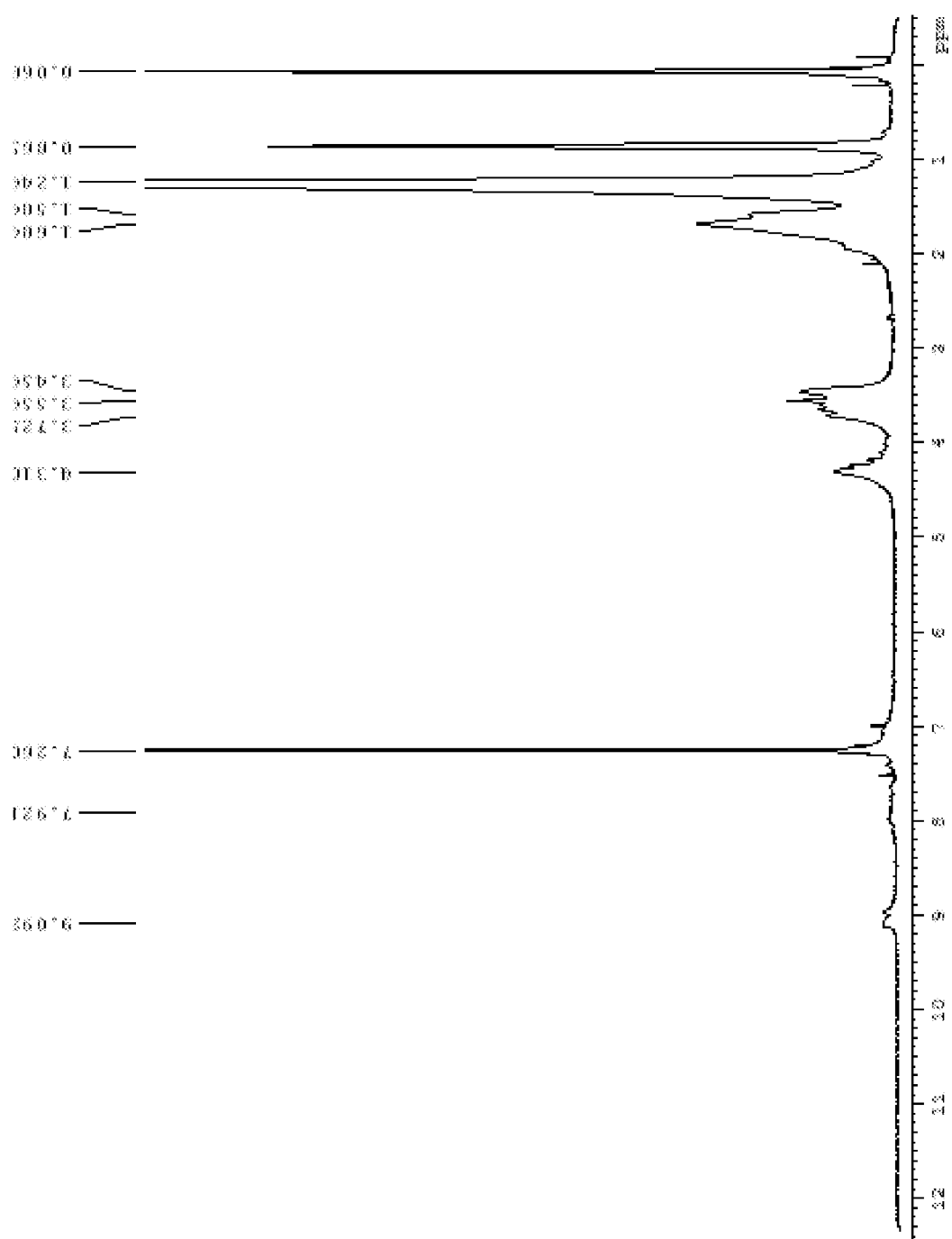
[Fig. 15]



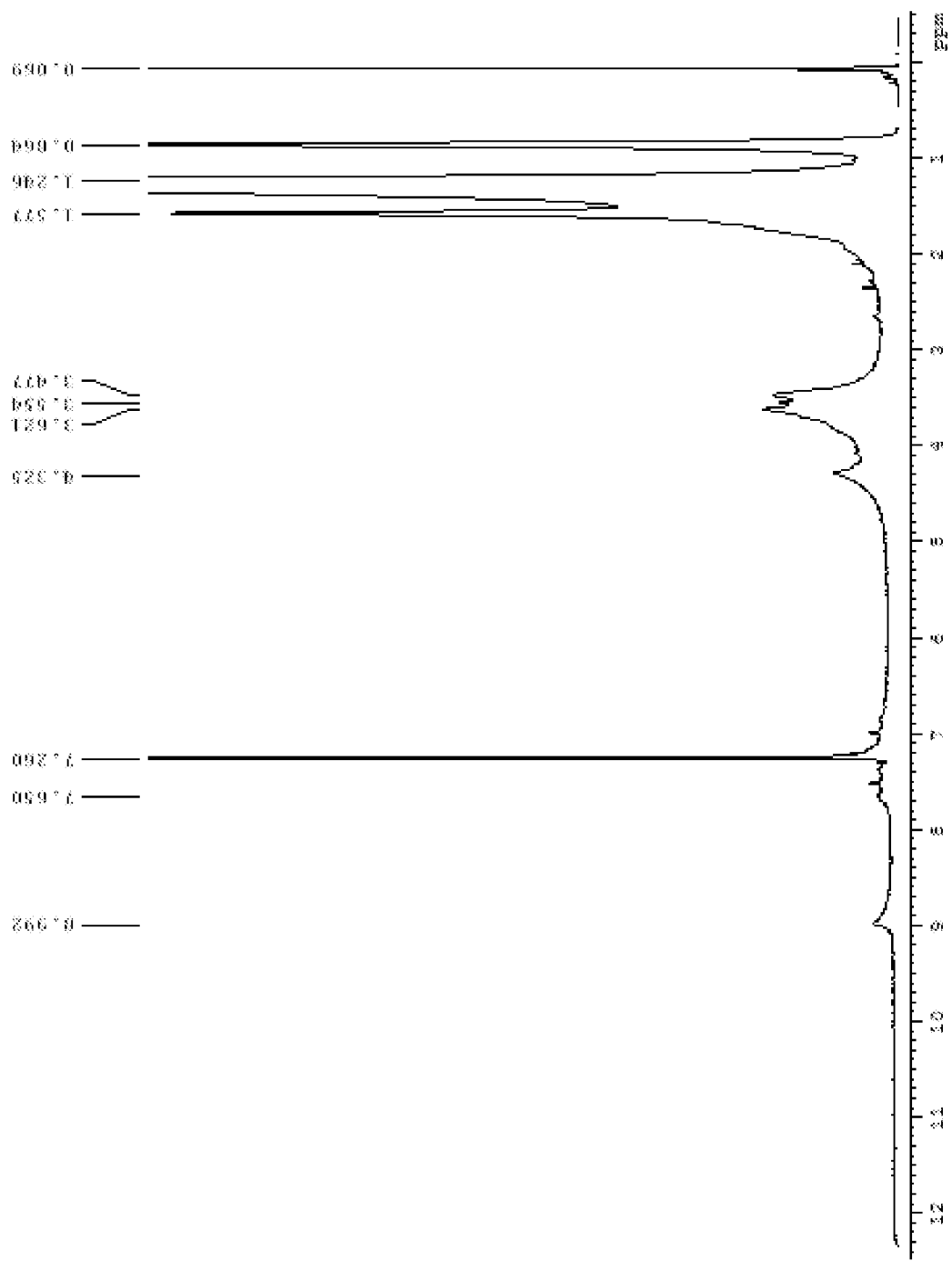
[Fig. 17]

Mass Spectrum SmartFormula Report									
Analysis Info					Acquisition Date 1/21/2014 10:00:17 AM				
Analysis Name D:\Data\Chemistry\Outside\IMRE\Y60116-4.d					Operator default user				
Method manhacq_APCI_POS.m					Instrument / Ser# micrOTOF-Q II 10289				
Sample Name Y60116-4									
Comment IMRE									
Acquisition Parameter									
Source Type		APCI		Ion Polarity		Positive		Set Nebulizer 3.0 Bar	
Focus		Not active		Set Capillary		4500 V		Set Dry Heater 200 °C	
Scan Begin		50 m/z		Set End Plate Offset		-500 V		Set Dry Gas 4.0 l/min	
Scan End		3000 m/z		Set Collision Cell RF		300.0 Vpp		Set Divert Valve Waste	
Mass, m/z	#	Formula		m/z	err (ppm)	ndb	e ⁻ Conf	N-Rule	
804.1870	1	C 35 H 52 Br 2 N 3 O 2 S 2		804.1862	-0.9	13.5	even	ok	
806.1860	1	C 35 H 52 Br N 3 O 2 S 2 *91Br		806.1842	-2.3	13.5	even	ok	

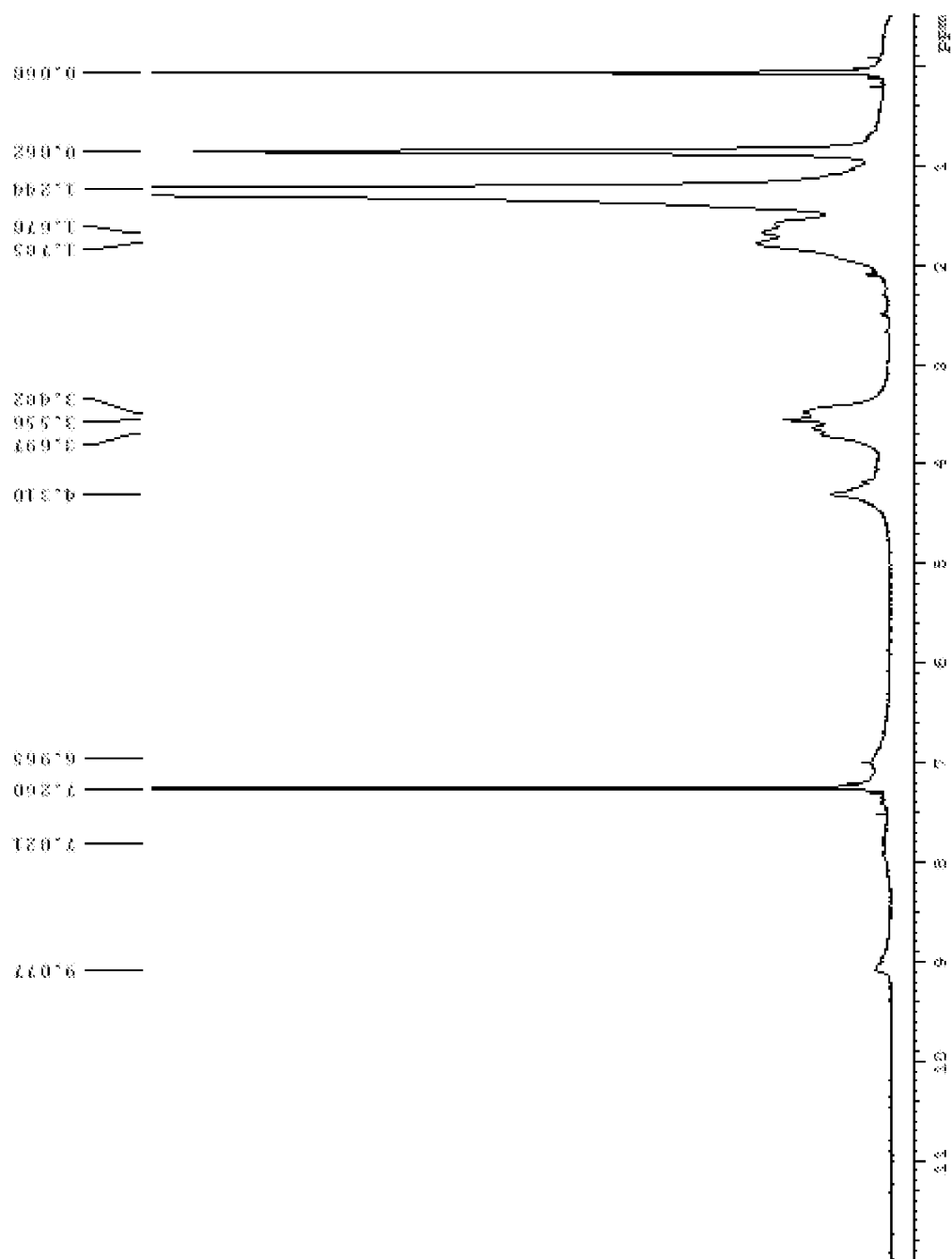




[Fig. 18]

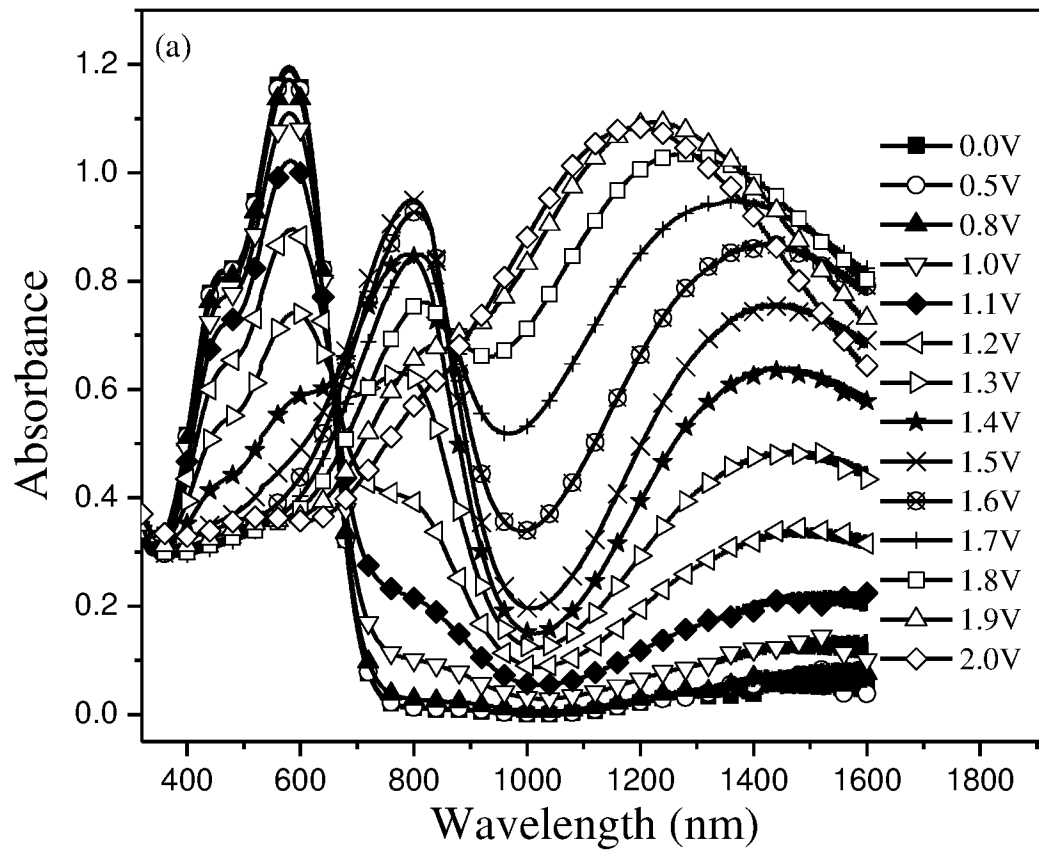


[Fig. 19]

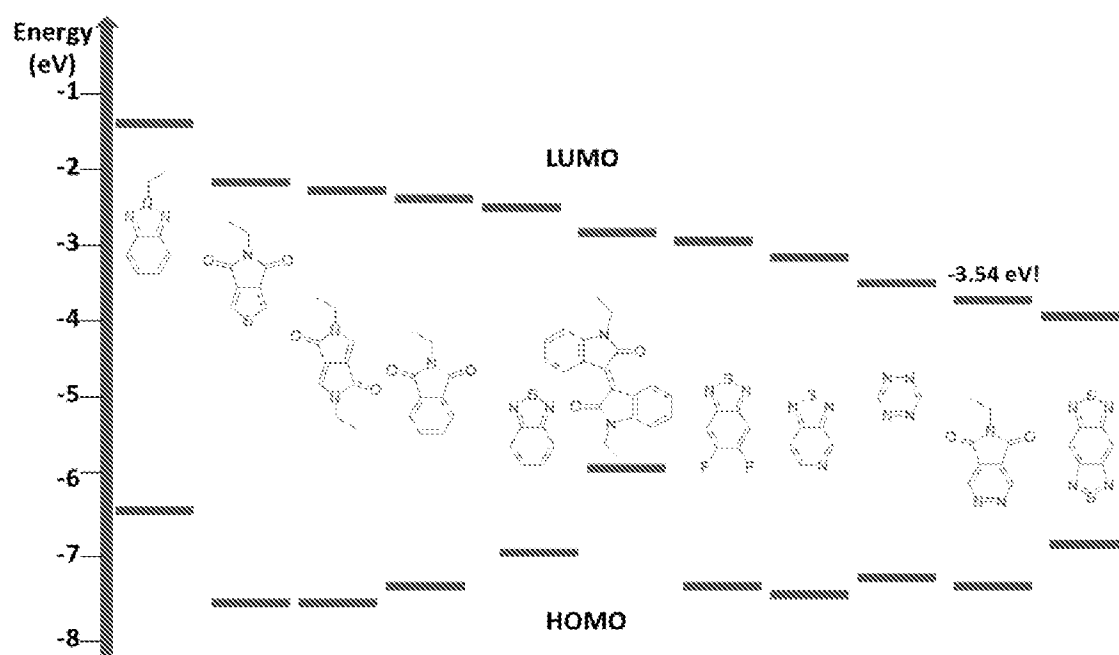


[Fig. 20]

[Fig. 21]

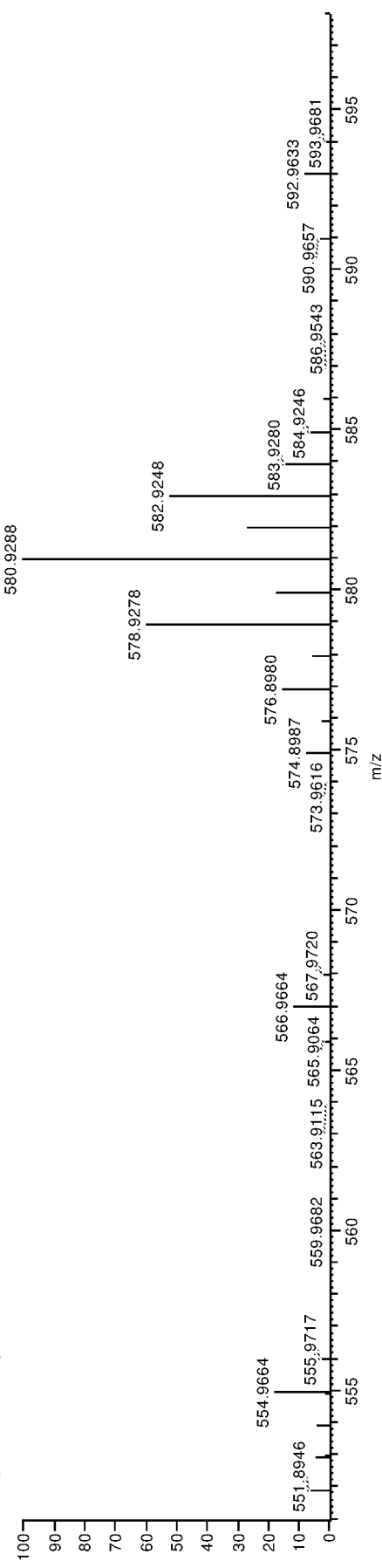


[Fig. 22]



[Fig. 23]

Jan14-YQ0116-2-c2-av#1 RT: 0.58
T: + c Full ms [550.91-597.97]
m/z= 578.50-583.30



Jan14-YQ0116-2-c2-av#1 RT: 0.58
T: + c Full ms [550.91-597.97]
m/z= 578.50-583.30

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
578.9278	4337317.0	59.80	578.9285	-1.21	14.0	C ₂₂ H ₁₉ O ₂ N ₃ ⁷⁹ Br ₂ ³² S ₂
580.9288	7252938.0	100.00	580.9265	3.94	14.0	C ₂₂ H ₁₉ O ₂ N ₃ ⁷⁹ Br ₁ ⁸¹ Br ₁ ³² S ₂
582.9248	3775662.0	52.06	582.9245	0.63	14.0	C ₂₂ H ₁₉ O ₂ N ₃ ⁸¹ Br ₂ ³² S ₂

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/SG2015/050218

A. CLASSIFICATION OF SUBJECT MATTER

**C07D 237/00 (2006.01) C07D 237/30 (2006.01) C08G 61/00 (2006.01) C08G 61/12 (2006.01) H01L 51/00 (2006.01)
 H01L 51/42 (2006.01)**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

GOOGLE SCHOLAR keywords (DONOR-ACCEPTOR; POLYMERS; PHTHALAZINE; PYRIDAZINE; PYRROLOPYRIDAZINE; AGENCY SCIENCE; YE; CHO; NEO; XU; and synonyms and associated terms)

ESPACENET keywords (DONOR; ACCEPTOR; POLYMERS; PHTHALAZINE; and PYRIDAZINE) combined with Applicant name (AGENCY FOR SCIENCE) or Inventor names (YE; CHO; NEO; and XU)

REGISTRY, CAPLUS: Sub-structure search based on present Formula (I) defined in claims 1 and incorporated in the polymeric structure defined in claim 2.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 18 September 2015	Date of mailing of the international search report 18 September 2015
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Steven Zammit AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0399359644

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Claims 1-2 (in full), 5-25 (in part), 26 (in full), 27-41 (in part), 42-81 (in full), 85-86 (in part), 87-91 (in full)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/SG2015/050218
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MARGETIC, D. ET AL., "Rigid Alicyclic Molecules from Bicyclo[2.2.1]hept-2-enes (=8,9,10-Trinorbornenes) and 1,4-Dipyridin-2-ylphthalazines as Stereoselective Coupling Agents", Helvetica Chimica Acta, 2009 , 92(2), p298-312 see page 300, Scheme 1	1, 5-7, 11, 20-23, 26-29, 35-41 and 85
X	LIGONG, L. ET AL., "A Direct Route to 4,5-Diazaphthalimides by the Unprecedented Reaction of Maleimides with <i>s</i> -Tetrazines", Electronic Conference on Heterocyclic Chemistry, 1998 , (1998), p394-405 see Scheme 4, compounds 9a-9c	1, 5-7, 11, 20-23, 26-29 and 35-36
X	HAIDER, N. ET AL., "Product class 8: pyridazines", Science of Synthesis, 2004 , 16, p125-249 see page 163, second compound in Table 5	1, 5-7, 11, 20-23, 26-29 and 35-36
X	WARRENER, R. N., "3,6-Di(2-pyridyl)- <i>sec</i> -tetrazine", e-EROS Encyclopedia of Reagents for Organic Synthesis, 2003 , p1-14 see pages 7-8	1, 5-7, 11, 20-23, 26-29 and 35-36
X	JP 2012-233098 A (KONICA MINOLTA HOLDINGS INC) 29 November 2012 see Abstract; and page 15, compounds 501-507	1-2, 5-36, 42-46, 49-78, 80 and 85-91
A	ICLI, M. ET AL., "Donor-Acceptor Polymer Electrochromes with Tunable Colors and Performance", Chemistry of Materials, 2010 , 22, p4034-4044 see whole document	1-2, 5-81 and 85-91

Supplemental Box

Continuation of: Box III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept. This Authority has found that there are different 3 inventions based on the following features that separate the claims into distinct groups:

Invention 1: Claims 1-2 (in full), 5-25 (in part), 26 (in full), 27-41 (in part), 42-81 (in full), 85-86 (in part), 87-91 (in full) are directed to compounds of Formula (I) or polymers of Formula (IV) which incorporate a common structural motif in their scaffold, derived from the compounds of Formula (I). These claims are also directed to the methods of preparing these compounds.

Invention 2: Claims 3 (in full), 5-25 (in part), 83-84 (in full), 85-86 (in part) are directed to compounds of Formula (VI) and methods of preparing these compounds.

Invention 3: Claims 4 (in full), 27-41 (in part), 82 (in full) and 85-86 (in part) are directed to compounds of Formula (VIIa) or (VIIb) and methods of preparing these compounds.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention. For Markush claims the requirement of a technical interrelationship and the same corresponding special technical features is considered to be met when all alternatives are of a similar nature. When the Markush grouping is for alternatives of chemical compounds, they are regarded as being of a similar nature where all alternatives have a common property or activity, and (i) a common structure is present, that is, a significant structural element is shared by all of the alternatives, or (ii) in cases where the common structure cannot be the unifying criteria, all alternatives belong to a recognized class of chemical compounds in the art to which the invention pertains.

The only feature common to invention 1 and 2 which provides a technical relationship among them is that the compounds of Formula (VI) (i.e. invention 2) are used as precursors for the preparation of compounds of Formula (I) (i.e. invention 1), via an inverse electron demand Diels-Alder reaction. The only feature common to inventions 1 and 3 which provides a technical relationship among them is the structural motif defined in Formulae (VIIa) or (VIIb). However, each one of these features is known in the art and is disclosed in prior art document D1 (DAVOR, M. ET AL., Helvetica Chimica Acta, **2009**, 92(2), p298-312). For example, Scheme 1 of D1 discloses the reaction of N-methylphthalimide (compound of Formula (VIIb)) with 3,6-dipyridin-2-yl-s-tetrazine (compound of Formula (VI)), via an inverse electron demand Diels-Alder reaction to provide a phthalazine derivative (compound No. 6). Therefore, in light of D1, each one of the common features fails to represent a special technical feature and thus the requirements for unity of invention are not satisfied *a posteriori*.

As a result of the lack of unity this Searching Authority has restricted the search and report to the first invention mentioned defined in claims 1-2, 5-81 and 85-91.

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/SG2015/050218	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
JP 2012-233098 A	29 November 2012	JP 2012233098 A	29 Nov 2012
		JP 5691810 B2	01 Apr 2015
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			