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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 February 2014 (27.02.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/029014 A1

(51) International Patent Classification:
C07D 517/04 (2006.01) *C08G 61/12* (2006.01)
C07D 491/048 (2006.01) *H01L 51/46* (2006.01)

(21) International Application Number:
PCT/CA2013/000736

(22) International Filing Date:
20 August 2013 (20.08.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/684,943 20 August 2012 (20.08.2012) US

(71) Applicant: **UNIVERSITÉ LAVAL** [CA/CA]; Vice-rectorat à la recherche et, à la création, Pavillon des Sciences de l'Education, 2320, rue des Bilbliothèques, Local 1434 Québec, Québec G1V 0A6 (CA).

(72) Inventors: **LECLERC, Mario**; 909, rue Laudance, Apt. 316, Québec, Québec G1X 5H7 (CA). **BEAUPRÉ, Serge**; 1150, rue de Constance, Québec, Québec G1Y 1K2 (CA).

(74) Agent: **BERESKIN & PARR LLP/ S.E.N.C.R.L., S.R.L.**; 40th Floor, 40 King Street West, Toronto, Ontario M5H 3Y2 (CA).

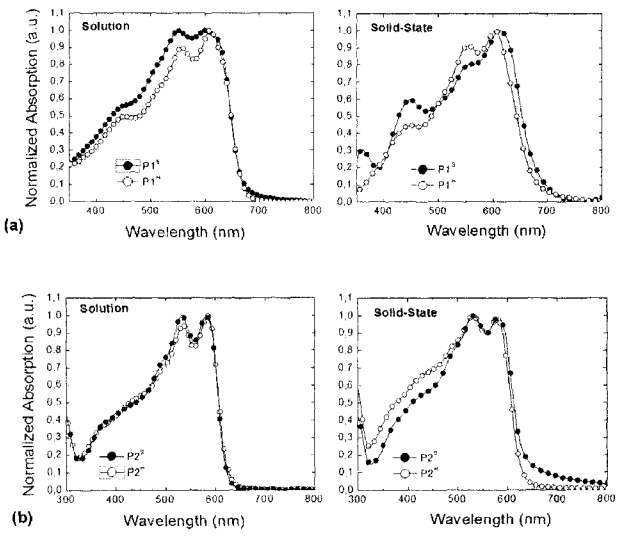
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

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

(54) Title: THIENO, FURO AND SELENOPHENO-[3,4-C]PYRROLE-4,6-DIONE COPOLYMERS

FIG. 3



(57) Abstract: Novel photoactive copolymers based on thieno, furo or selenopheno-[3,4- c]pyrrole-4,6-dione-derivative are described herein. More specifically, the photoactive copolymers comprise repeating units of Formula I -[A^1-A^2]- I wherein A1 is an electron donating unit such as a mono or polycyclic heteroaryl that is unsubstitued or substituted with one or more C_{1-20}-alkyl or C_{1-20}-alkoxy; and A^2 is an alkylfuro or alkylselenopheno-[3,4-c]pyrrole-4,6-dione-derivative. The photoactive copolymers are suitable for use in BHJ solar cells.

WO 2014/029014 A1

TITLE THIENO, FURO AND SELENOPHENO-[3,4-C]PYRROLE-4,6-DIONE COPOLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority from co-pending U.S. Provisional Application No. 61/684,943 filed on August 20, 2012, the contents of which are incorporated herein by reference in their entirety.

FIELD

[0002] The present specification broadly relates to thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione copolymers. More specifically, but not exclusively, the present specification relates to thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione copolymers and their use in electro-optical applications. The present specification also relates to a process for the preparation of thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione copolymers.

BACKGROUND

[0003] Harvesting the unlimited and renewable energy from sunlight to produce electricity through photovoltaic devices represents a promising way to address growing global energy needs while minimizing detrimental effects on the environment. Among all photovoltaic technologies, polymer bulk heterojunction (BHJ) solar cells offer a compelling option for tomorrow's photovoltaic devices since they can be easily prepared using low-cost and energy efficient roll-to-roll manufacturing processes.[1-9] During the past several years, the development of new classes of conjugated copolymers, combined with optimization of device fabrication, led to significant improvements of the power conversion efficiency of bulk heterojunction (BHJ) solar cells.[10-13]

[0004] Lately, *push-pull* copolymers based on a thieno[3,4-*c*]pyrrole-4,6-dione (TPD) repeat unit distinguished themselves as being among the most efficient materials for bulk heterojunction solar cells with power conversion efficiencies exceeding 8%.[13-23] A significant amount of work has subsequently been done in order to tune the band gap of *push-pull* TPD-based copolymers by

using several co-monomers with different electron-donating strengths. Carbazoles,[24-25] bithiophenes,[18, 23, 26] benzodithiophenes,[14-16, 22] cyclopentadithiophenes,[27-30] dithienosiloles[17, 19, 31-32] and dithienogermoles[20, 33] led to copolymers with band gaps ranging from 1.5 to 2.2 eV.

[0005] Long or branched side chains have been added to TPD co-monomers to promote the solubility of the copolymers[34-35]. Comparative studies between oligo- and poly(*n*-alkylfuran)s[36-38] poly(*n*-alkylselenophene)s[39-41] and poly(*n*-alkylthiophene)s[42] have shown that the nature of the heteroatom in the heterocycle may have a strong influence on their solubility, intermolecular interactions and optical and electronic properties.

[0006] The present specification refers to a number of documents, the contents of which are herein incorporated by reference in their entirety.

SUMMARY

[0007] The present specification broadly relates to thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers.

[0008] In an embodiment, the present specification relates to a photoactive copolymer comprising first and second co-monomer repeat units, wherein the first co-monomer repeat unit comprises an electron donating unit and wherein the second co-monomer repeat unit comprises a thieno, furo or selenopheno-[3,4-c]pyrrole-4,6-dione-derivative.

[0009] In an embodiment, the present specification relates to a photoactive copolymer comprising first and second co-monomer repeat units, wherein the first co-monomer repeat unit comprises an electron donating unit and wherein the second co-monomer repeat unit comprises a furo or selenopheno-[3,4-c]pyrrole-4,6-dione-derivative.

[0010] In an embodiment, the present specification relates to a photoactive copolymer comprising repeating units of Formula I:

$$-[A^1-A^2]- \quad \text{I}$$

[0011] wherein A^1 is an electron donating unit and A^2 is an alkylfuro or alkylselenopheno-[3,4-c]pyrrole-4,6-dione-derivative.

[0012] In an embodiment, the present specification relates to a photoactive copolymer comprising repeating units of Formula II:

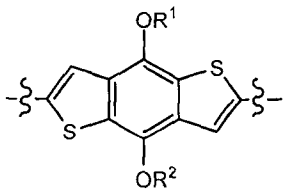
$$-[A^1-A^{2"}]- \quad \text{II}$$

[0013] wherein A^1 is an electron donating unit and $A^{2"}$ is an alkylthieno, alkylfuro or alkylselenopheno-[3,4-c]pyrrole-4,6-dione-derivative.

[0014] In an embodiment, the present specification relates to a photoactive copolymer comprising from 5 to 1000000 repeating units.

[0015] In an embodiment A^1 is a mono or polycyclic heteroaryl that is unsubstitued or substituted with one or more C_{1-20}-alkyl or C_{1-20}-alkoxy.

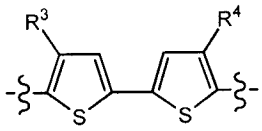
[0016] In a further embodiment, A^1 is a fused tricyclic heteroaryl that is substituted with one or more C_{1-20}-alkoxy. In a further embodiment, A^1 is a fused tricyclic heteroaryl that is substituted with 1, 2, 3, 4, 5 or 6 C_{1-20}-alkoxy. In a further embodiment, A^1 is a fused tricyclic heteroaryl that is substituted with 1, 2, 3 or 4 C_{1-20}-alkoxy. In a further embodiment, A^1 is a fused tricyclic heteroaryl having the structure:



[0017] wherein R^1 and R^2 are independently selected from H and C_{1-20}-alkyl. In a further embodiment, R^1 and R^2 are independently selected from C_{1-20}-alkyl. In a further embodiment, R^1 and R^2 are the same.

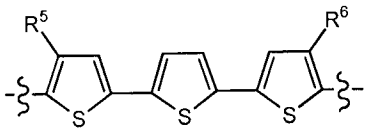
[0018] In a further embodiment, A^1 is a bicyclic heteroaryl that is substituted with one or more C_{1-20}-alkyl. In a further embodiment, A^1 is a bicyclic heteroaryl

that is substituted with 1, 2, 3, 4, 5 or 6 C_{1-20}-alkyl. In a further embodiment, A^1 is a bicyclic heteroaryl that is substituted with 1, 2, 3 or 4 C_{1-20}-alkyl. In a further embodiment, the individual cyclic rings in the bicyclic aryl are linked via a single bond. In a further embodiment, A^1 is a bicyclic heteroaryl having the structure:



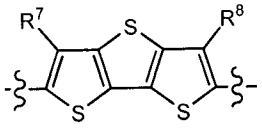
[0019] wherein R^3 and R^4 are independently selected from C_{1-20}-alkyl.

[0020] In a further embodiment, A^1 is a tricyclic heteroaryl that is substituted with one or more C_{1-20}-alkyl. In a further embodiment, A^1 is a tricyclic heteroaryl that is substituted with 1, 2, 3, 4, 5 or 6 C_{1-20}-alkyl. In a further embodiment, A^1 is a tricyclic heteroaryl that is substituted with 1, 2, 3 or 4 C_{1-20}-alkyl. In a further embodiment, the individual cyclic rings in the tricyclic aryl are linked via a single bond. In a further embodiment, A^1 is a tricyclic heteroaryl having the structure:



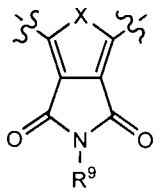
[0021] wherein R^5 and R^6 are independently selected from C_{1-20}-alkyl.

[0022] In a further embodiment, A^1 is a fused tricyclic heteroaryl that is substituted with one or more C_{1-20}-alkyl. In a further embodiment, A^1 is a fused tricyclic heteroaryl that is substituted with 1, 2, 3, 4, 5 or 6 C_{1-20}-alkyl. In a further embodiment, A^1 is a fused tricyclic heteroaryl that is substituted with 1, 2, 3 or 4 C_{1-20}-alkyl. In a further embodiment, A^1 is a fused tricyclic heteroaryl having the structure:



[0023] wherein R^7 and R^8 are independently selected from C_{1-20}-alkyl.

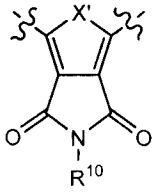
[0024] In an embodiment, A^2 is a monomer of the Formula III:



III

[0025] wherein X is selected from O and Se; and R^9 is selected from C_{1-20}-alkyl.

[0026] In an embodiment, $A^{2''}$ is a monomer of the Formula IV:



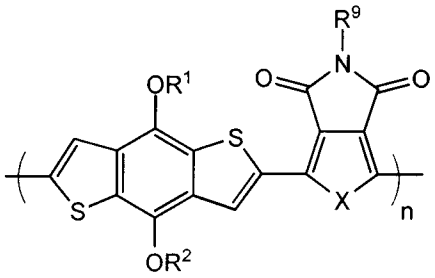
IV

[0027] wherein X' is selected from O, S and Se; and R^{10} is selected from C_{1-20}-alkyl.

[0028] In an embodiment, R^1 and R^2 are independently selected from C_{5-18}-alkyl. In a further embodiment, $R^1$and R^2 are independently selected from C_{5-15}-alkyl. In a further embodiment R^1 and R^2 are the same and are selected from C_5-alkyl, C_6-alkyl, C_7-alkyl, C_8-alkyl, C_9-alkyl and C_{10}-alkyl. In a further embodiment R^1 and R^2 are the same and are selected from branched C_5-alkyl, C_6-alkyl, C_7-alkyl, C_8-alkyl, C_9-alkyl and C_{10}-alkyl.

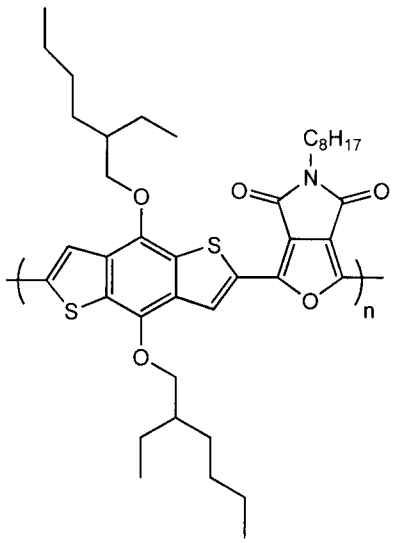
[0029] In an embodiment, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are independently selected from C_{5-20}-alkyl. In a further embodiment, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are independently selected from C_{12}-alkyl, C_{13}-alkyl, C_{14}-alkyl, C_{15}-alkyl, C_{16}-alkyl, C_{17}-alkyl, C_{18}-alkyl, C_{19}-alkyl and C_{20}-alkyl.

[0030] In an embodiment, the present specification relates to a photoactive copolymer having the structure:



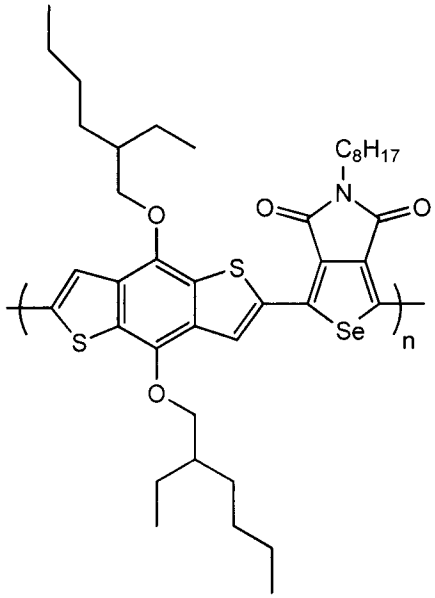
[0031] wherein R^1, R^2 and R^9 are independently selected from H and C_{1-20}-alkyl; X is selected from O and Se; and n is an integer ranging from 5 to 1000000.

[0032] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



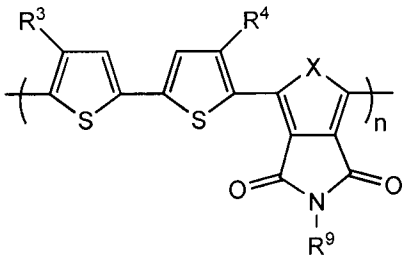
[0033] wherein n is an integer ranging from 5 to 1000000.

[0034] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



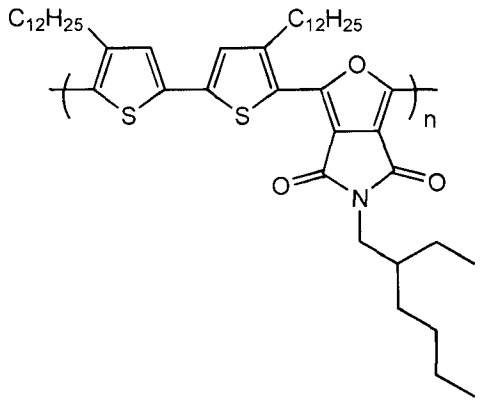
[0035] wherein n is an integer ranging from 5 to 1000000.

[0036] In an embodiment, the present specification relates to a photoactive copolymer having the structure:



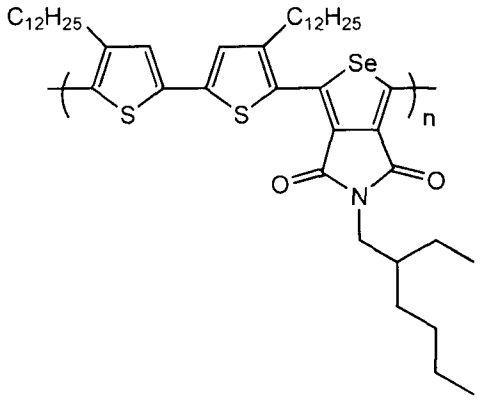
[0037] wherein R^3, R^4 and R^9 are independently selected from H and C_{1-20}-alkyl; X is selected from O and Se; and n is an integer ranging from 5 to 1000000.

[0038] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



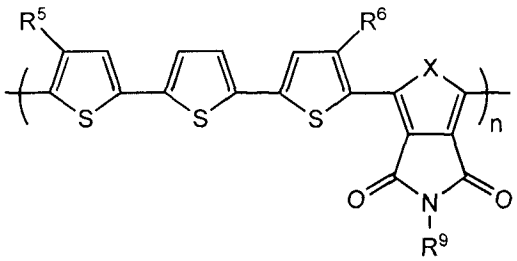
[0039] wherein n is an integer ranging from 5 to 1000000.

[0040] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



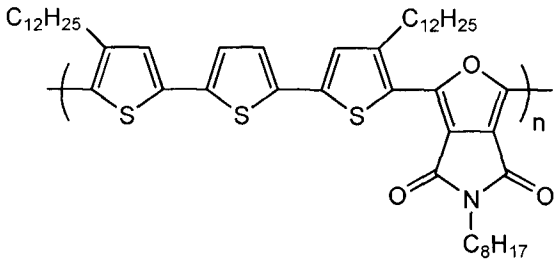
[0041] wherein n is an integer ranging from 5 to 1000000.

[0042] In an embodiment, the present specification relates to a photoactive copolymer having the structure:



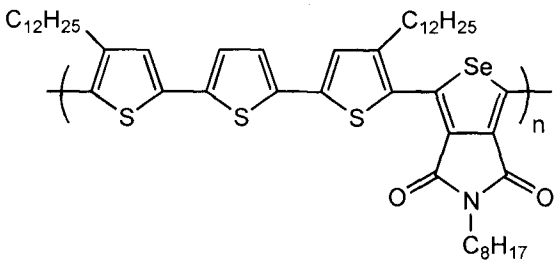
[0043] wherein R^5, R^6 and R^9 are independently selected from H and C_{1-20}-alkyl; X is selected from O and Se; and n is an integer ranging from 5 to 1000000.

[0044] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



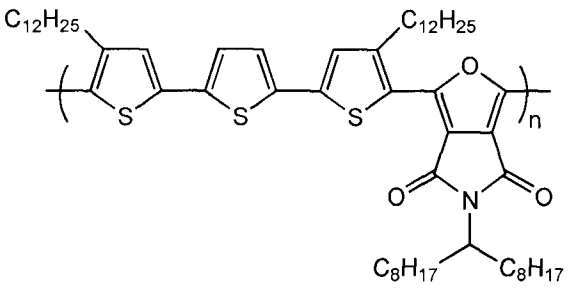
[0045] wherein n is an integer ranging from 5 to 1000000.

[0046] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



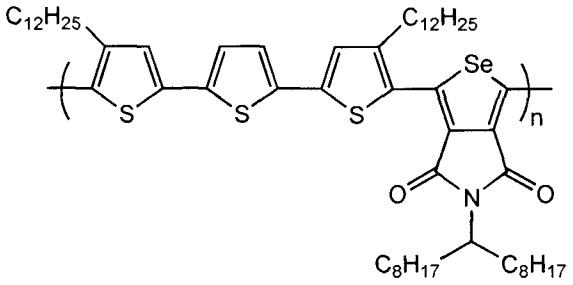
[0047] wherein n is an integer ranging from 5 to 1000000.

[0048] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



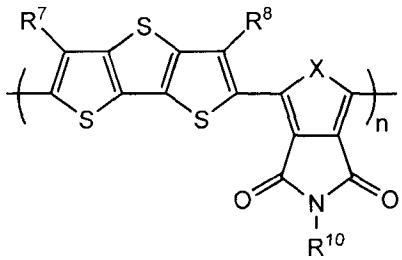
[0049] wherein n is an integer ranging from 5 to 1000000.

[0050] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



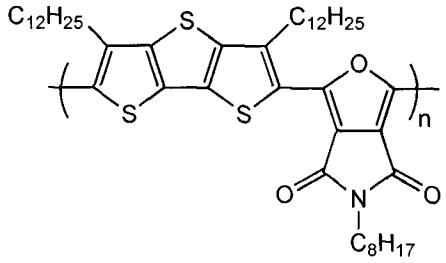
[0051] wherein n is an integer ranging from 5 to 1000000

[0052] In an embodiment, the present specification relates to a photoactive copolymer having the structure:



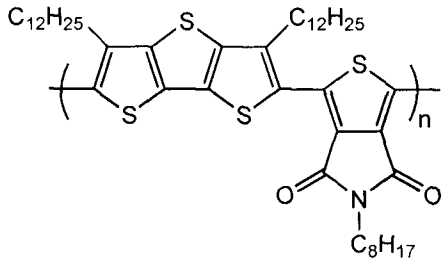
[0053] wherein R^7, R^8 and R^{10} are independently selected from H and C_{1-20}-alkyl; X is selected from O, S and Se; and n is an integer ranging from 5 to 1000000. In a further embodiment, R^7, R^8 and R^{10} are independently selected from H and C_{1-20}-alkyl; X is selected from O and Se; and n is an integer ranging from 5 to 1000000.

[0054] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



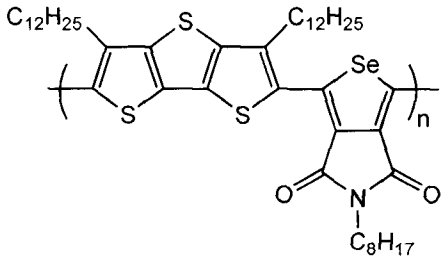
[0055] wherein n is an integer ranging from 5 to 1000000.

[0056] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



[0057] wherein n is an integer ranging from 5 to 1000000.

[0058] In a particular embodiment, the present specification relates to a photoactive copolymer having the structure:



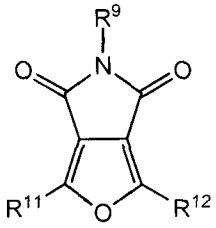
[0059] wherein n is an integer ranging from 5 to 1000000.

[0060] In an embodiment, the present specification relates to thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers suitable for use in bulk heterojunction solar cells. In one aspect, these copolymers exhibit broad absorption spectra, reduced band gaps and deep HOMO/LUMO energy levels.

[0061] In an embodiment, the present specification relates to thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers for use in electronic devices. In an aspect, non-limiting examples of electronic devices include organic electronic devices, including photovoltaic devices, OLEDs (organic light emitting devices), OPVs (organic photovoltaics), transistors, OFETs (organic filed effect transistors), batteries, and printed electronics generally, as well as sensors.

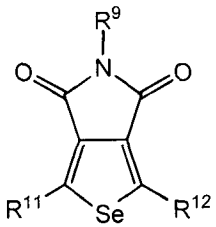
[0062] In an embodiment, the present specification relates to furo[3,4-*c*]pyrrole-4,6-dione (FPD) and selenopheno[3,4-*c*]pyrrole-4,6-dione (SePD) derivatives.

[0063] In a particular embodiment, the present specification relates to an alkylfuro[3,4-c]pyrrole-4,6-dione derivative having the structure:



[0064] wherein R^9 is H or C_{1-20}-alkyl; and R^{11} and R^{12} are independently selected from H and halogen. In a further particular embodiment, R^9 is C_{1-20}-alkyl and R^{11} and R^{12} are both H. In a further particular embodiment, R^9 is C_{1-20}-alkyl and R^{11} and R^{12} are both Br.

[0065] In a particular embodiment, the present specification relates to an alkylselenopheno[3,4-c]pyrrole-4,6-dione derivative having the structure:

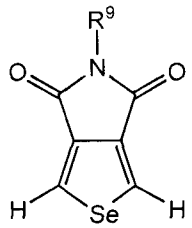


[0066] wherein R^9 is H or C_{1-20}-alkyl; and R^{11} and R^{12} are independently selected from H and halogen. In a further particular embodiment, R^9 is C_{1-20}-alkyl

and R^{11} and R^{12} are both H. In a further particular embodiment, R^9 is C_{1-20}-alkyl and R^{11} and R^{12} are both Br.

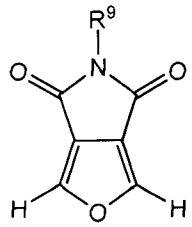
[0067] In an embodiment, the present specification relates to a process for preparing alkylfuro[3,4-*c*]pyrrole-4,6-dione (FPD) and alkylselenopheno[3,4-*c*]pyrrole-4,6-dione (SePD) derivatives.

[0068] In an embodiment, the present specification relates to a process for preparing a selenopheno[3,4-c]pyrrole-4,6-dione derivative having the structure:



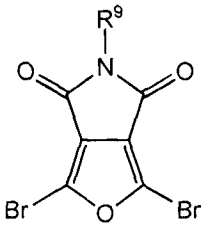
[0069] wherein R^9 is H or C_{1-20}-alkyl, the process comprising heating a reaction mixture comprising selenophene-3,4-dicarboxylic acid and an amine or alkylamine under conditions to provide the selenopheno[3,4-c]pyrrole-4,6-dione derivative.

[0070] In an embodiment, the present specification relates to a process for preparing a furo[3,4-c]pyrrole-4,6-dione derivative having the structure:



[0071] wherein R^9 is H or C_{1-20}-alkyl, the process comprising reacting furan-3,4-dicarbonyl dichloride and an amine or an alkylamine under conditions to provide the furo[3,4-c]pyrrole-4,6-dione derivative.

[0072] In an embodiment, the present specification relates to a process for preparing a furo[3,4-c]pyrrole-4,6-dione derivative having the structure:



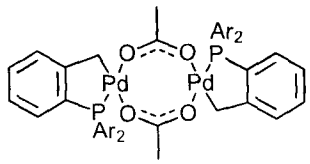
[0073] wherein R^9 is H or C_{1-20}-alkyl, the process comprising reacting 2,5-dibromo-furan-3,4-dicarbonyl dichloride and an amine or alkylamine under conditions to provide the alkylfuro[3,4-c]pyrrole-4,6-dione derivative.

[0074] In an embodiment the alkylamine is C_{1-20}-alkyl-NH_2. In a further embodiment, the amine is NH_3 or an equivalent therefore.

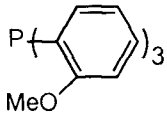
[0075] In an embodiment, the present specification relates to a process for preparing thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers. In a further embodiment, the present specification relates to a process for preparing furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers. In a particular embodiment of the present specification, the copolymers are prepared by copolymerizing a furo[3,4-c]pyrrole-4,6-dione (FPD) or a selenopheno[3,4-c]pyrrole-4,6-dione (SePD) derivative (*pull*-unit) with a suitable *push*-unit. In a further particular embodiment of the present specification, the copolymers are prepared by either Stille cross-coupling reactions or direct heteroarylation polymerization.[35] In yet a further particular embodiment of the present specification, the copolymers are prepared by catalytic direct heteroarylation polymerization.[35]

[0076] In an embodiment, the present specification relates to a process for preparing furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers, the process comprising reacting an activated furo or selenopheno-[3,4-c]pyrrole-4,6-dione-derivative and a suitable electron donating moiety in the presence of one or more catalysts and one or more ligands under conditions for direct heteroarylation polymerization of the furo or selenopheno-[3,4-c]pyrrole-4,6-dione-derivative and the electron donating moiety, to provide the furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers. In a further embodiment of the present

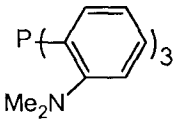
specification, the electron donating moiety is a mono or polycyclic heteroaryl that is unsubstitued or substituted with one or more C_{1-20}-alkyl or C_{1-20}-alkoxy groups. In a further embodiment of the present specification, the one or more catalysts are palladium (II) catalysts. In a further embodiment of the present specification, the one or more ligands are trialkyl or triaryl phosphines, in which the alkyl and aryl groups are substituted or unsubstituted, or the corresponding phosphonium salts, or complexes thereof with metals. In a further embodiment of the present specification, the one or more ligands are selected from: $P(t\text{-}Bu)_3HBF_4$, $P(Cy)_3HBF_4$, $P(t\text{-}Bu)_2MeHBF_4$, $P(o\text{-}tol)_3$,



Ar = o-tolyl



and



.

[0077] The foregoing and other objects, advantages and features of the present specification will become more apparent upon reading of the following non-restrictive description of illustrative embodiments thereof, given by way of example only with reference to the accompanying drawings/figures.

BRIEF DESCRIPTION OF THE DRAWINGS/FIGURES

[0078] In the appended drawings/figures:

[0079] **FIG. 1** is an illustration of the molecular structure of selected *push* co-monomers in accordance with an embodiment of the present disclosure.

[0080] **FIG. 2** is an illustration of the molecular structure of selected thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers (*push-pull* co-polymers) in accordance with an embodiment of the present disclosure.

[0081] **FIG. 3** is an illustration of the effect of the molecular weight on the absorption spectra of: **a)** $P1^S$ vs $P1^H$; and **b)** $P2^S$ vs $P2^H$ in accordance with an embodiment of the present disclosure.

[0082] **FIG. 4** is an illustration of the effect of the heteroatom on the absorption spectra of: **a)** $P1^S$, $P2^S$ and $P3^S$; and **b)** $P8^H$ vs $P9^H$ in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

I. Glossary

[0083] In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this specification pertains.

[0084] Unless otherwise indicated, the definitions and embodiments described in this and other sections are intended to be applicable to all embodiments and aspects of the application herein described for which they are suitable as would be understood by a person skilled in the art.

[0085] The word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one", but it is also consistent with the meaning of "one or more", "at least one", and "one or more than one" unless the content clearly dictates otherwise. Similarly, the word "another" may mean at least a second or more unless the content clearly dictates otherwise.

[0086] As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "include" and "includes") or "containing" (and any form of containing, such as "contain" and "contains"), are inclusive or open-ended and do not exclude additional, unrecited elements or process steps.

[0087] As used in this specification and claim(s), the word "consisting" and its derivatives, are intended to be close ended terms that specify the presence of

stated features, elements, components, groups, integers, and/or steps, and also exclude the presence of other unstated features, elements, components, groups, integers and/or steps.

[0088] The term "consisting essentially of", as used herein, is intended to specify the presence of the stated features, elements, components, groups, integers, and/or steps as well as those that do not materially affect the basic and novel characteristic(s) of features, elements, components, groups, integers, and/or steps.

[0089] The terms "about", "substantially" and "approximately" as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least ±1% of the modified term if this deviation would not negate the meaning of the word it modifies.

[0090] The term "suitable" as used herein means that the selection of the particular compound or conditions would depend on the specific synthetic manipulation to be performed, and the identity of the molecule(s) to be transformed, but the selection would be well within the skill of a person trained in the art. All process/method steps described herein are to be conducted under conditions sufficient to provide the product shown or named. A person skilled in the art would understand that all reaction conditions, including, for example, reaction solvent, reaction time, reaction temperature, reaction pressure, reactant ratio and whether or not the reaction should be performed under an anhydrous or inert atmosphere, can be varied to optimize the yield of the desired product and it is within their skill to do so.

[0091] The expression "proceed to a sufficient extent" as used herein with reference to the reactions or process steps disclosed herein means that the reactions or process steps proceed to an extent that conversion of the starting material or substrate to product is maximized. Conversion may be maximized when greater than about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 99% of the starting material or substrate is converted to product.

[0092] As used herein, the term "*push-pull*" copolymer refers to copolymers in which electron-donating (ED) and electron-accepting (EA) groups interact via a pi-conjugated system such that a partial intermolecular charge transfer occurs from the donor group to the acceptor group through the conjugated path. Intramolecular charge transfer induces an asymmetric polarization of the ground state and can provide push-pull copolymers with large ground-state dipole moments.

[0093] As used herein, the term "pull moiety" refers to an electron withdrawing group (EWG) which has its usual meaning in the art, and refers to a moiety having a relatively high electronegativity and thus a relatively strong tendency to attract or receive electron density from more electron-rich moieties. Non-limiting examples of electron withdrawing groups include NO_2, C(O)R, halogens and CN.

[0094] As used herein, the term "push moiety" refers to an electron donating group (EDG) and has its usual meaning in the art, and refers to a moiety having a relatively low electronegativity and thus a relatively strong tendency to donate electron density to less electron-rich moieties. Non-limiting examples of electron donating groups include alkyl, alkoxy, amino and hydroxy/

[0095] As used herein, the term "derivative" refers to a structural analog and designates a compound having a structure similar to that of another one, but differing from it in respect of a certain component. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, or substructures. A structural analog can be imagined to be formed, at least theoretically, from the other compound. Despite a high chemical similarity, structural analogs are not necessarily functional analogs and can have very different physical, chemical, biochemical, or pharmacological properties.

[0096] The present description refers to a number of chemical terms and abbreviations used by those skilled in the art. Nevertheless, definitions of selected terms are provided for clarity and consistency.

[0097] Abbreviations: NMR: Nuclear Magnetic Resonance; MS: Mass Spectrometry; m.p.: melting point; HRMS: High Resolution Mass Spectrometry; SEC: Size-Exclusion Chromatography; M_n: Number Average Molecular Weight; PDI: PolyDispersity Index; DP: Degree of Polymerization; EtOAc: Ethyl Acetate; CH_2Cl_2: Dichloromethane (DCM); $CDCl_3$: Chloroform-d; TFA: Trifluoroacetic acid; AcOH: Acetic acid; TLC: Thin Layer Chromatography; FCC: Flash Column Chromatography.

[0098] As used herein, the term "alkyl" embraces straight-chain or branched-chain hydrocarbons. Substituted alkyl residues can be substituted in any suitable position. Examples of alkyl groups containing from 1 to 20 carbon atoms are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl and octadecyl, nonadecane and eicosane, the n-isomers of all these residues, isopropyl, isobutyl, isopentyl, neopentyl, isohexyl, isodecyl, 3-methylpentyl, 2,3,4-trimethylhexyl, sec-butyl, tert-butyl, or tert-pentyl.

[0099] As used herein, the term "lower alkyl" embraces straight-chain or branched-chain saturated hydrocarbons containing 1, 2, 3, 4, 5 or 6 carbon atoms. Substituted alkyl groups can be substituted in any suitable position. Examples of lower alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, neopentyl, and hexyl.

[00100] As used herein, the term "alkylene" embraces a linear saturated divalent hydrocarbon group of one to six carbon atoms or a branched-chain saturated divalent hydrocarbon group of three to six carbon atoms. Examples of alkylene groups are methylene, ethylene, 2,2-dimethylethylene, propylene, 2-methylpropylene, butylene, and pentylene.

[00101] As used herein, the terms “alkoxy” or “alkyloxy” embraces an alkyl group attached to the parent molecular group through an oxygen atom.

[00102] As used herein, the term "aryl" embraces an aromatic group which is a single ring or multiple rings fused, bridged or linked together via single bond.

When formed of multiple rings, at least one of the constituent rings is aromatic. In an embodiment, aryl substituents include phenyl, indanyl, biphenyl and naphthyl.

[00103] The term "halo" means the halogens fluorine, chlorine, bromine or iodine.

[00104] The term "heterocyclo" as used herein embraces saturated and partially unsaturated heteroatom-containing cyclic groups, where the heteroatoms are selected from nitrogen, oxygen, sulfur, and selenium. The heterocyclo groups are either monocyclic, bicyclic, tricyclic or quadracyclic, provided they have a suitable number of atoms, for example from 3 to 30 atoms, and are stable. A bicyclic, tricyclic or quadracyclic heterocyclo group can be fused, bridged and/or simply linked via a single bond. Examples of saturated heterocyclo groups include saturated 3 to 6-membered heteromonocyclic groups containing 1 to 4 nitrogen atoms (e.g. pyrrolidinyl, imidazolidinyl, piperidino, piperazinyl, etc.); saturated 3 to 6-membered heteromonocyclic groups containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms (e.g. morpholinyl, etc.); saturated 3 to 6-membered heteromonocyclic groups containing 1 to 2 sulfur atoms and 1 to 3 nitrogen atoms (e.g., thiazolidinyl, etc.). Examples of partially unsaturated heterocyclo groups include dihydrothiophene, dihydropyran, dihydrofuran and dihydrothiazole.

[00105] The term "heteroaryl" as used herein embraces fully unsaturated or aromatic heterocyclo groups. The heteroaryl groups are either monocyclic, bicyclic, tricyclic or quadracyclic, provided they have a suitable number of atoms, for example from 3 to 30 atoms, and are stable. A bicyclic, tricyclic or quadracyclic heteroaryl group is fused, bridged and/or simply linked via a single bond. Examples of heteroaryl groups include unsaturated 3 to 6 membered heteromonocyclic groups containing 1 to 4 nitrogen atoms, for example, pyrrolyl, pyrrolinyl, imidazolyl, pyrazolyl, pyridyl, pyrimidyl, pyrazinyl, pyridazinyl, triazolyl (*e.g.*, 4H-1,2,4-triazolyl, 1H-1,2,3-triazolyl, 2H-1,2,3-triazolyl, etc.), tetrazolyl (e.g. 1H-tetrazolyl, 2H-tetrazolyl, etc.), etc.; unsaturated condensed heterocyclo groups containing 1 to 5 nitrogen, oxygen and/or sulfur atoms include, for example, indolyl, isoindolyl, indolizinyl, benzimidazolyl, quinolyl, isoquinolyl, indazolyl,

benzotriazolyl, tetrazolopyridazinyl (*e.g.*, tetrazolo[1,5-b]pyridazinyl, etc.), etc.; unsaturated 3 to 6-membered heteromonocyclic groups containing an oxygen atom, include, for example, pyranyl, furyl, etc.; unsaturated 3 to 6-membered heteromonocyclic groups containing a sulfur or a selenium atom, include for example, thienyl, selenophene-yl, etc.; unsaturated 3- to 6-membered heteromonocyclic groups containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, include, for example, oxazolyl, isoxazolyl, oxadiazolyl (*e.g.*, 1,2,4-oxadiazolyl, 1,3,4-oxadiazolyl, 1,2,5-oxadiazolyl, etc.) etc.; unsaturated condensed heterocyclo groups containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms (*e.g.* benzoxazolyl, benzoxadiazolyl, etc.); unsaturated 3 to 6-membered heteromonocyclic: groups containing 1 to 2 sulfur atoms and 1 to 3 nitrogen atoms, include, for example, thiazolyl, thiadiazolyl (*e.g.*, 1,2,4-thiadiazolyl, 1,3,4-thiadiazolyl, 1,2,5-thiadiazolyl, etc.) etc.; unsaturated condensed heterocyclo groups containing 1 to 2 sulfur atoms and 1 to 3 nitrogen atoms (*e.g.*, benzothiazolyl, benzothiadiazolyl, etc.), unsaturated linked 5 or 6-membered heteromonocyclic: groups containing 1 to 2 sulfur atoms and/or 1 to 3 nitrogen atoms, include, for example, bithienyl and trithienyl and the like. The term also embraces groups where heterocyclo groups are fused with aryl groups. Examples of such fused bicyclic groups include benzofuran, benzothiophene, benzopyran, and the like.

[00106] **Monomers and Copolymers**

[00107] Exemplary synthetic routes for preparing thieno-[3,4-*c*]pyrrole-4,6-dione (TPD)[14,23], furo-[3,4-*c*]pyrrole-4,6-dione (FPD) and selenopheno-[3,4-*c*]pyrrole-4,6-dione (SePD) co-monomers, in accordance with an embodiment of the present specification, are depicted in **Schemes 1** to **4**. Furan-3,4-dicarboxylic acid **(5)** was prepared in high yield (97%) by the saponification of the commercially available dimethyl-3,4-furan dicarboxylate **(4)** (**Scheme 2**). Furan-3,4-dicarboxylic acid **(5)** was treated with oxalyl chloride to provide furan-3,4-dicarbonyl dichloride **(6)** according to known literature procedures.[43] 5-Alkylfuro-[3,4-*c*]pyrrole-4,6-dione (FPD) co-monomers **(7a-c)** [suitable for direct heteroarylation polymerization (DHAP)] were prepared in low yields using the

melting state procedure reported for the synthesis of 1,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione.[44] Bromination at the 1,3-positions of the 5-alkylfuro[3,4-c]pyrrole-4,6-dione co-monomers **(7a-c)** using classical bromination procedures, non-limiting examples of which include Br_2, NBS and DBI, did not provide the desired products and instead led to unwanted side reactions such as ring opening of the furan moiety.

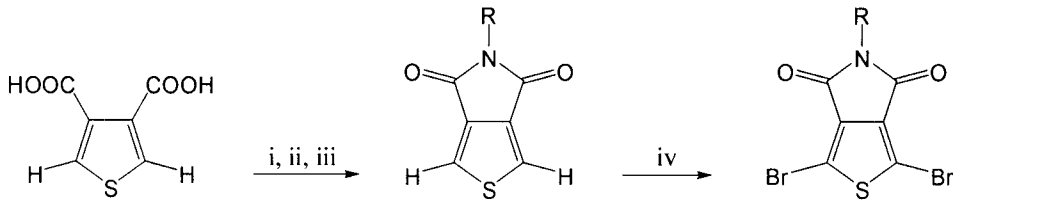
[00108] To circumvent the stability issues of the 5-alkylfuro[3,4-c]pyrrole-4,6-dione during the bromination reaction, a novel synthetic route was developed to achieve the desired brominated products (**Scheme 3**). Dimethyl 2,5-dibromofuran-3,4-dicarboxylate **(8)** was prepared from furan in three steps according to reported literature procedures.[45] Saponification of compound **8** provided 2,5-dibromo-furan-3,4-dicarboxylic acid **(9)**. Treatment of compound **9** with oxalyl chloride provided 2,5-dibromo-furan-3,4-dicarbonyl dichloride **(10)**. 2,5-Dibromo-furan-3,4-dicarbonyl dichloride **(10)** was subsequently reacted with *n*-octylamine (melted state) to afford 1,3-dibromo-5-octyl-furo[3,4-*c*]pyrrole-4,6-dione **(11)** which proved suitable for Stille cross-coupling polymerization.

[00109] Selenophene-3,4-dicarboxylic acid **(12)** was prepared in three steps from commercially available selenophene (**Scheme 4**).[46] 5-Octyl-selenopheno[3,4-*c*]pyrrole-4,6-dione **(13)** was prepared following a synthetic procedure previously developed for the synthesis of low-cost TPD co-monomers.[47] Selenophene-3,4-dicarboxylic acid **(12)** and *n*-octylamine were mixed and reacted in the melted state. This novel synthetic route reduces the number of chemical steps and avoids the need for two highly reactive chemicals (*i.e.* thionyl chloride or oxalyl chloride) typically involved in the synthesis of 5-alkylthieno[3,4-*c*]pyrrole-4,6-dione derivatives.[14] Bromination of 5-octylselenopheno[3,4-c]pyrrole-4,6-dione **(13)** using N-bromosuccinimide in a mixture of H_2SO_4/trifluoroacetic acid successfully provided 1,3-dibromo-5-octyl-selenopheno[3,4-*c*]pyrrole-4,6-dione **(14)**.

[00110] Previous work on thieno[3,4-*c*]pyrrole-4,6-dione-based copolymers showed that direct heteroarylation polymerization (DHAP) significantly reduces the

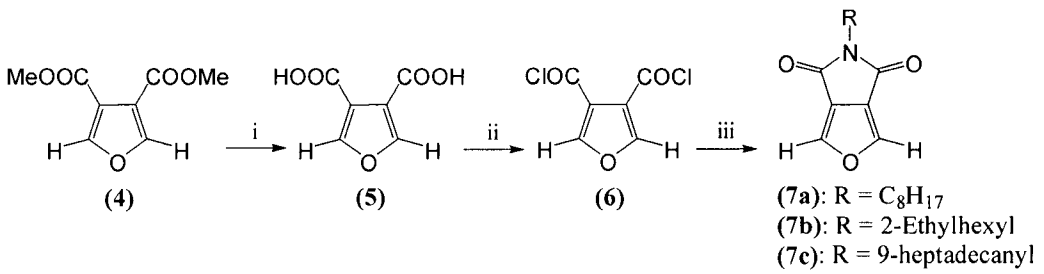
number of chemical steps and leads to higher molecular weights when compared to analogs made by Stille cross coupling polymerization.[35] Stille and DHAP polymerization methods were used for the synthesis of several new *push-pull* copolymers **P1-P11** (**FIG. 2**) based on the *push* co-monomers illustrated in **FIG. 1** and the *pull* co-monomers based on: 1) thieno[3,4-*c*]pyrrole-4,6-dione (TPD); 2) furo[3,4-*c*]pyrrole-4,6-dione (FPD); and 3) selenopheno[3,4-c]pyrrole-4,6-dione (SePD). The synthesis of the *push-pull* copolymers **P1-P11**, in accordance with an embodiment of the present specification, is illustrated in **Schemes 5** and **6**. The molecular structures of the *push-pull* copolymers **P1-P11** are summarized in **FIG. 2**.

[00111] **Synthesis of thieno[3,4-c]pyrrole-4,6-dione (TPD) co-monomers.**



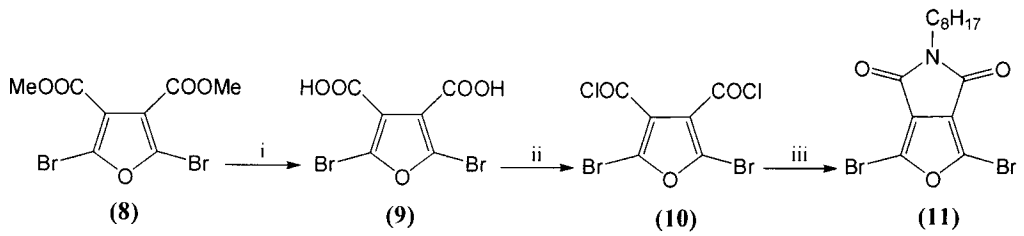
SCHEME 1 - Reagents and conditions: (i) Ac_2O, 140°C, overnight; (ii) R-NH_2, toluene, reflux 24h; (iii) $SOCl_2$, reflux, 12h; (iv) NBS, H_2SO_4/CF_3COOH, r. t. overnight.

[00112] **Synthesis of furo[3,4-*c*]pyrrole-4,6-dione (FPD) co-monomers.**



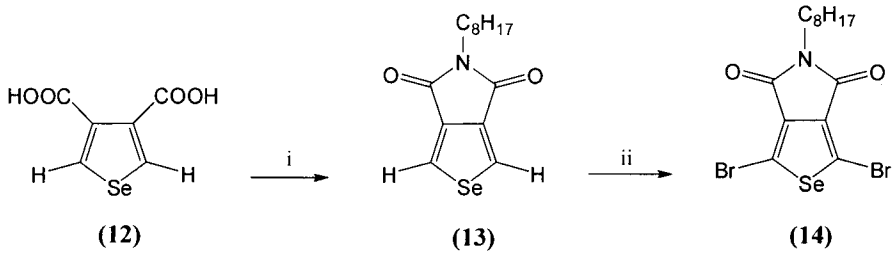
Scheme 2: Reagents and conditions: (i) KOH, EtOH, reflux; (ii) oxalyl chloride, reflux; (iii) R-NH_2, 140 °C, 2h.

[00113] **Synthesis of 1,3-dibromo-5-octylfuro[3,4-*c*]pyrrole-4,6-dione.**



Scheme 3: Reagents and conditions: (i) KOH, EtOH, reflux; (ii) oxalyl chloride, reflux; (iii) *n*-octylamine, 140 °C, 2h.

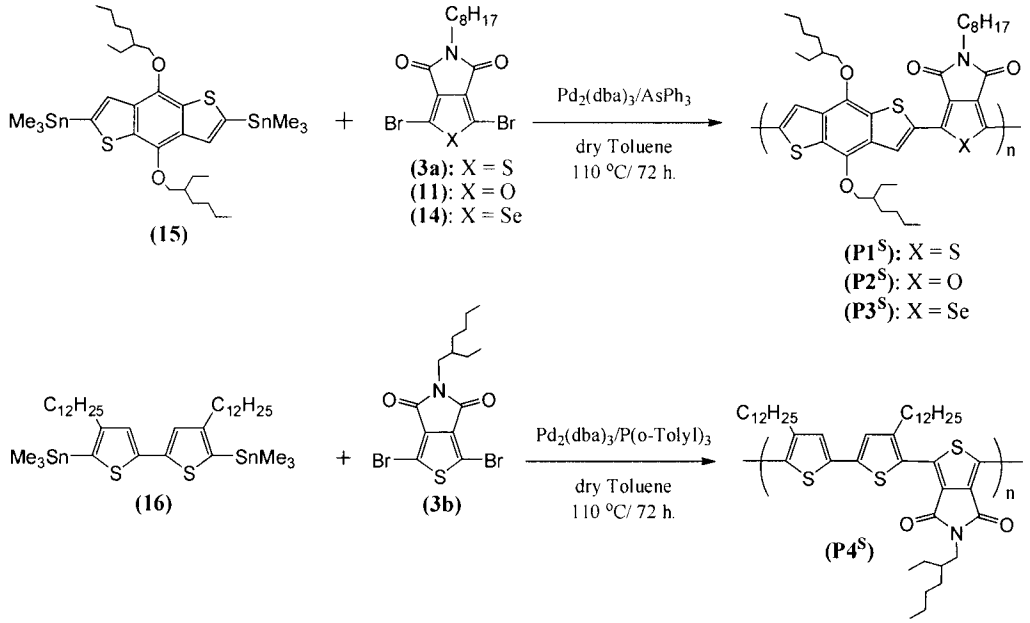
[00114] **Synthesis of 5-octyl-selenopheno[3,4-*c*]pyrrole-4,6-dione (SePD).**



Scheme 4: Reagents and conditions: i) *n*-octylamine, 200 °C; ii) NBS, H_2SO_4/CF_3COOH, r. t. overnight.

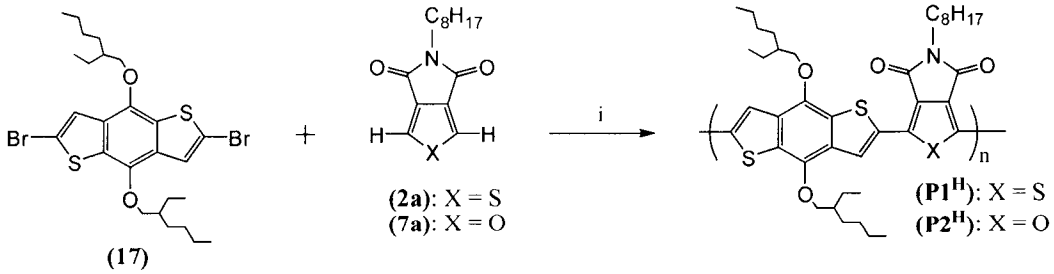
[00115] Thieno[3,4-*c*]pyrrole-4,6-dione-based copolymers **P1^S** and **P4^S** (**Scheme 5**) were prepared according to known literature procedures (Stille cross coupling polymerization) and used as benchmarks since these two *push-pull* copolymers are among the most efficient materials in bulk heterojunction solar cells with power conversion efficiencies of 7.1% and 7.3% respectively [18, 22].

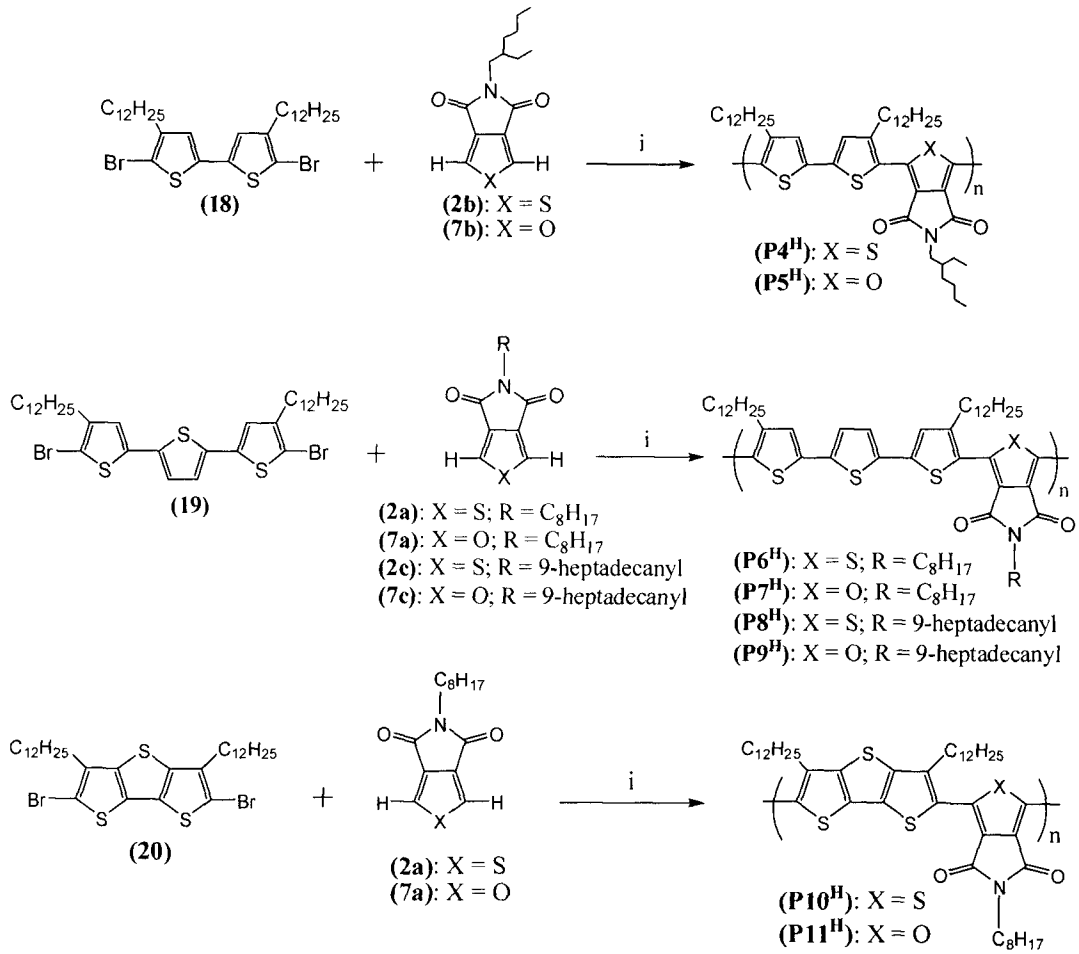
[00116] Synthesis of Copolymers P1^S-P4^S by Stille Cross-Coupling Polymerization.



Scheme 5

[00117] Synthesis of Copolymers P1^H-P2^H- and P4^H-P11^H by Direct Heteroarylation Polymerization (DAHP)





Scheme 6: Reagents and conditions: i) *trans*-di(μ -acetato)-bis[*o* -(di-*o*-tolyl-phosphino)benzyl]dipalladium(II) (4% mol), *tris*(o-methoxyphenyl)phosphine (8% mol), Cs_2CO_3 (2 eq.), pivalic acid (30% mol), dry Toluene, 120 °C, 24-36 h.

[00118] **Molecular Weights**

[00119] All polymers were characterized by size exclusion chromatography (SEC) using the monodisperse polystyrene standard in hot 1,2,4-trichlorobenzene (TCB). Data are summarized in **Table 1**.

[00120] Direct heteroarylation polymerization (DHAP) has proven to be a clean and efficient polymerization method, yielding high molecular weight materials.[35] Following careful optimization of the Stille polymerization parameters, it was found that the number-average molecular weight of $\mathbf{P1}^{S}$ hit a plateau at M_n = 20 kDa. On the other hand, direct heteroarylation polymerization (DHAP) led to a higher number-average molecular weight for $\mathbf{P1}^{H}$ (M_n = 51 kDa). An enhancement of the number-average molecular weights using DHAP instead of Stille cross-coupling polymerization was also observed for $\mathbf{P2}^{S}$ vs $\mathbf{P2}^{H}$ and $\mathbf{P4}^{S}$ vs $\mathbf{P4}^{H}$. Since molecular weights are known to modulate certain properties of conjugated polymers such as solubility, crystallinity and charge mobility, it was surmised that $\mathbf{P1}^{H}$, $\mathbf{P2}^{H}$ and $\mathbf{P4}^{H}$ would be promising materials for bulk heterojunction solar cells. The versatility of the direct heteroarylation polymerization (DHAP) method was further demonstrated by the synthesis of additional *push-pull* conjugated copolymers $\mathbf{P5}^{H}$-$\mathbf{P11}^{H}$. It was observed that the heteroatom (oxygen vs sulfur) has an effect on the solubility of the polymer. According to the literature, it appears that oligofurans are more soluble than their oligothiophene analogues.[37] The precipitation of $\mathbf{P6}^{H}$ (M_n = 10 kDa) during the polymerization reaction in hot toluene could be observed whereas $\mathbf{P7}^{H}$ (M_n = 16 kDa) remained in solution for the entire polymerization time (24h). Precipitation of polymers during the polymerization reaction prevents chain growth and limits molecular weights. Finally, optimized polymerization conditions led to higher number average molecular weights [$\mathbf{P8}^{H}$ (M_n = 41 kDa)] than those observed for non-optimized polymerization [$\mathbf{P9}^{H}$ (M_n = 21 kDa)]. $\mathbf{P10}^{H}$ (M_n = 14 kDa) and $\mathbf{P11}^{H}$ (M_n = 17 kDa) displayed similar number-average molecular weights. The FPD-based copolymers were again found to be more soluble than their TPD analogues.

[00121] **Optical and Electronic Properties**

[00122] The electro-optical properties of all copolymers are summarized in **Table 2**. Despite relatively large optical band gaps (ranging from 1.77 eV to 1.97 eV), all polymers displayed a broad UV-Vis absorption spectra which is of paramount importance for efficient absorption of the solar spectral flux in bulk heterojunction solar cells. The effect of the heteroatom (sulfur, oxygen, and selenium) on the optical properties of the copolymers was investigated by comparing TPD- to FPD- and SePD-based copolymers.

[00123] The effect of molecular weights on the optical properties is negligible since they are all within the same range, except for **P1** and **P2**. As reported in **Table 1**, it was observed that direct heteroarylation polymerization leads to higher molecular weights than Stille cross-coupling polymerization. The UV-Vis of $\mathbf{P1}^{S}$ vs $\mathbf{P1}^{H}$ and $\mathbf{P2}^{S}$ vs $\mathbf{P2}^{H}$ are illustrated in **FIGs. 3a, b**. Similarities between the UV-Vis spectra of both low and high molecular weights polymers are observed. The saturation of the optical properties means that the effective conjugation length was already reached for the so-called low molecular weight materials. The UV-Vis spectra of $\mathbf{P1}^{S}$, $\mathbf{P2}^{S}$ and $\mathbf{P3}^{S}$ are shown in **FIG. 4a**. The effect of the heteroatom on the optical properties is rather small. The substitution of the sulfur atom ($\mathbf{P1}^{S}$) by oxygen ($\mathbf{P2}^{S}$) led to a hypsochromic shift of both the maximum of absorption (29 nm) and the band gap (0.10 eV). According to the literature, a furan ring is smaller than a thiophene ring due to the smaller size and higher electronegativity of the oxygen atom.[37] The lone electron pairs are more localized on the oxygen atom than on the sulfur atom which makes furan less aromatic than thiophene.[37] Moreover, the C-O bond (1.362 Å) is smaller than the C-S bond (1.714 Å). Since *n*-alkylfuro[3,4-c]pyrrole-4,6-dione (FPD) and *n*-alkylthieno[3,4-c]pyrrole-4,6-dione (TPD) are, from a chemical perspective, substituted furans and thiophenes, one can reason that FPD derivatives may be weaker *pull* moieties when compared to their TPD counterparts, resulting in higher band gaps for *push-pull* FPD-based copolymers. Indeed, the optical band gap of $\mathbf{P2}^{S}$ (E_g^{opt} = 1.90 eV) is larger than $\mathbf{P1}^{S}$ (E_g^{opt} = 1.80 eV). A noticeable increase of the oxidation potential for $\mathbf{P2}^{S}$ was also observed compared to $\mathbf{P1}^{S}$, resulting in a stabilization of the HOMO energy

level of 0.09 eV for $\mathbf{P2^S}$ vs $\mathbf{P1^S}$. As shown in **Table 2**, for most TDP/FPD copolymer pairings, a hypsochromic shift of the optical band gap and a stabilization of the HOMO energy level for FPD-based copolymers were observed (**FIG. 4b**). Furthermore, it has been shown that the incorporation of a heavier atom such as selenium narrows the band gap due to a stabilization of the LUMO energy level.[48] The effect of the selenium atom ($\mathbf{P3^H}$) on the electro-optical properties was observed to be rather small. A bathochromic shift of the maximum of absorption (25 nm) and a small reduction of the band gap (0.03 eV) for $\mathbf{P3^S}$ when compared to $\mathbf{P1^S}$ (**FIG. 4a**) was observed. Unlike polyselenophene/polythiophene analogues, no stabilization of the LUMO level was observed for SePD copolymers (**Table 2**). Since the electronegativity of sulfur (2.58) and selenium (2.55) is substantially identical, one can reason that SePD and TPD have the same *pull* strength.

[00124] **EXPERIMENTAL**

[00125] A number of examples are provided herein below illustrating the preparation of furo[3,4-*c*]pyrrole-4,6-dione (FPD) and selenopheno[3,4-*c*]pyrrole-4,6-dione (SePD) derivatives as well as thieno, furo and selenopheno-[3,4-c]pyrrole-4,6-dione copolymers. The following non-limiting examples are illustrative of the present disclosure.

[00126] **Materials**

[00127] ***Chemicals***: Thiophene-3,4-dicarboxylic acid **(1)** was purchased from Frontier Scientific Inc. Dimethyl furan-3,4-dicarboxylate **(4)** was purchased from Aldrich. Thieno[3,4-*c*]pyrrole-4,6-dione co-monomers **(2a-c; 3a-c)**,[14,23] furan-3,4-dicarboxylic acid **(5)**,[43] furan-3,4-dicarbonyl dichloride **(6)**,[43] dimethyl 2,5-dibromofuran-3,4-dicarboxylate **(8)**,[45] selenophene-3,4-dicarboxylic acid **(12)**,[46] 2,6-bis(trimethyltin)-4,8-di(2-ethylhexyloxyl)-benzo[1,2-b:3,4-b]dithiophene **(15)**,[14] (4,4'-didodecyl-2,2'-bithiophene-5,5'-diyl)-bis(trimethylstannane) **(16)**,[18] 2,6-dibromo-4,8-di(2-ethylhexyloxyl)-benzo[1,2-b:3,4-b]-dithiophene **(17)**,[49], 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene **(18)**,[18] 5,5''-dibromo-4,4''-didodecyl-2,2';5',2''-terthiophene **(19)**[23] and 2,6-dibromo-3,5-didodecylbisthieno[3,2-b:2',3'-

d]thiophene **(20)**[50] were prepared according to literature procedures. THF was distilled over sodium/benzophenone and acetonitrile was distilled over CaH_2 prior to use.

[00128] ***Instrumentation/Characterization***: ^1H and ^{13}C NMR spectra were recorded using a Varian Inova 400 MHz or Brucker AC 300 MHz in deuterated chloroform solution at 298 °K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) using a Varian Polymer Laboratories GPC220 equipped with an RI detector and a PL BV400 HT Bridge Viscometer. The column set consists of 2 PLgel Mixed C (300 x 7.5 mm) columns and a PLgel Mixed C guard column. The flow rate was fixed at 1.0 mL/min using 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) as eluent. The temperature of the system was set to 110°C. The samples were prepared at a concentration of nominally 1.0 mg/mL in hot TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vial was held at 110°C with stirring for 1 h for complete dissolution. The solution was filtered through a 2 µm porous stainless steel filter into a 2 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards dissolved in TCB. UV-vis-NIR absorption spectra were recorded using a Varian Cary 500 UV-vis-NIR spectrophotometer with 1 cm path length quartz cells. Spin-coated films on glass plates were used for solid-state UV-vis-NIR measurements. Optical bandgaps were determined from the onset of the absorption band (solid state). Cyclic voltammograms (CV) were recorded on a Solartron 1287 potentiostat using platinum wires as working electrode and counter-electrode at a scan rate of 50 mV/s. A polymer film was deposited on the working electrode. The reference electrode was Ag/Ag^+ (0.01 M of $AgNO_3$ in acetonitrile) and the electrolyte was a solution of 0.1 M of tetrabutylammonium tetrafluoborate in dry acetonitrile. Under these conditions, the oxidation potential of Ferrocene was 0.09 V versus Ag/Ag^+, whereas the oxidation potential of Ferrocene was 0.41 V versus SCE. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets (where the current differs from the baseline) assuming that the SCE electrode is -4.7 eV from vacuum.

[00129] ***Synthesis of 5-(octyl)-furo[3,4-c]pyrrole-4,6-dione (7a)***: A mixture of *n*-octylamine (0.46 mL, 2.7 mmol) and furan-3,4-dicarbonyl dichloride **(6)** (0.51g, 2.6 mmol) was heated to 140°C for 2h. The mixture was cooled down to room temperature. Ethyl acetate was added and the organic layer was washed with saturated sodium carbonate (2x). The organic layer was dried over sodium sulfate and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent DCM/Hexane 2:1) to afford 0.27g (Y = 34%) of the title compound as white solid. **m.p.** 111-113°C; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ: 7.75 (s, 2H); 3.58 (t, 2H, *J* = 7.3 Hz); 1.62 (m, 2H); 1.29 (m, 10H); 0.87 (t, 3H, *J* = 7.4 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ: 161.70; 138.60; 122.48; 38.58; 31.72; 29.10 (2C); 28.33; 26.80; 22.57; 13.99. **Elemental analysis** calculated as $C_{14}H_{19}N_1O_3$: C, 67.45; H, 7.68; N, 5.62; found: C, 67.96; H; 7.96; N, 5.54; **HRMS**: calculated: 249.1365; found: 249.1371.

[00130] ***Synthesis of 5-(2-ethylhexyl)-furo[3,4-c]pyrrole-4,6-dione (7b)***: A mixture of 2-ethylhexylamine (2.2 mL, 13.6 mmol) and furan-3,4-dicarbonyl dichloride **(6)** (2.50g, 12.9 mmol) was heated to 140°C for 2h. The mixture was cooled down to room temperature. Ethyl acetate was added and the organic layer was washed with saturated sodium carbonate (2x). The organic layer was dried over sodium sulfate and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent DCM/Hexane 2:1) to afford 1.10g (Y = 34%) of the title compound as white solid. **m.p.** 82-84°C; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ: 7.75 (s, 2H); 3.48 (d, 2H, *J* = 7.3 Hz); 1.78 (m, 1H); 1.32 (m, 8H); 0.89 (m, 6H,); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ: 161.94; 138.60; 122.39; 42.41; 38.01; 30.43; 28.39; 23.78; 22.92; 13.94; 10.32. **Elemental analysis** calculated as $C_{14}H_{19}N_1O_3$: C, 67.45; H, 7.68; N, 5.62; found: C, 67.50; H; 7.72; N, 5.63; **HRMS**: calculated (MNa+): 272.1257; found: 272.1259.

[00131] ***Synthesis of 5-(9-heptadecanyl)-furo[3,4-c]pyrrole-4,6-dione (7c)***: A mixture of heptadecan-9-amine (3.44g, 13.5 mmol) and furan-3,4-dicarbonyl dichloride **(6)** (2.47g, 12.8 mmol) was heated to 140°C for 2h. The mixture was cooled down to room temperature. Ethyl acetate was added and the

organic layer was washed with saturated sodium carbonate (2x). The organic layer was dried over sodium sulfate and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent DCM/Hexane 2:1) to afford 1.12g (Y = 23%) of the title compound as off-white solid. **m.p.** 32-33°C; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ: 7.73 (s, 2H); 4.08 (m, 1H,); 2.02 (m, 2H); 1.62 (m, 2H); 1.22 (m, 24H,); 0.88 (t, 3H, *J* = 7.3 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ: 162.09; 138.47; 122.23; 52.75; 32.09; 31.79; 29.42; 29.24; 29.17; 26.61; 22.61; 14.03. **Elemental analysis** calculated as $C_{23}H_{37}N_1O_3$: C, 73.56; H, 9.93; N, 3.73; found: C, 73.95; H; 10.26; N, 3.68; **HRMS** (MNa+): calculated: 398.2671; found: 398.2671.

[00132] ***Synthesis of 2,5-dibromofuran-3,4-dicarboxylic acid (9)***: A mixture of dimethyl 2,5-dibromofuran-3,4-dicarboxylate **(8)** (0.600g, 1.8 mmol) and potassium hydroxide (0.369g, 6.6 mmol) in ethanol (44 mL) was stirred and heated at reflux for 3 h. The mixture was cooled to room temperature and concentrated under reduced pressure to leave a solid which was dissolved in water. The resulting solution was acidified to pH = 1 with aqueous HCl (6M), then saturated with sodium chloride prior to extraction with ethyl acetate (2 x 100 mL). The organic extracts were combined and dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure to afford 0.49g (Y = 89%) of the title product as an off-white solid. **m.p.** 199-200°C; **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ: 161.57, 130.75, 119.25. **Elemental analysis** calculated as $C_6H_2Br_2O_5$: C, 22.96; H, 0.64; found: C, 22.94; H; 0.63; **HRMS** (MH+): calculated: 311.8269 Found: 311.8275.

[00133] ***Synthesis of 2,5-dibromofuran-3,4-dicarbonyl dichloride (10)***: Oxalyl chloride (6.5 mL, 76.5 mmol) was slowly added to 2,5-dibromofuran-3,4-dicarboxylic acid **(9)** (0.400g, 1.3 mmol). The mixture was heated to reflux for 2h and then cooled to room temperature. The volatiles were removed under reduced pressure, and the product was used without any further purification.

[00134] ***Synthesis of 1,3-dibromo-5-(octyl)-furo[3,4-c]pyrrole-4,6-dione (11)***: A mixture of n-octylamine (0.25 mL, 1.4 mmol) and 2,5-dibromo-furan-3,4-

dicarbonyl dichloride **(10)** (0.447g, 1.27 mmol) was heated to 140°C for 1h. The mixture was cooled down to room temperature. Ethyl acetate was added and the organic layer was washed with saturated sodium carbonate. The organic layer was dried over sodium sulfate and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent DCM/Hexane 2:1) to afford 0.14g (Y = 27%) of the title compound as white solid. **m.p.** 113-115°C; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ: 3.58 (t, 2H, *J* = 7.3 Hz); 1.62 (m, 2H); 1.29 (m, 10H); 0.87 (t, 3H, *J* = 7.4 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ: 159.46; 123.87; 120.25; 38.97; 31.76; 29.10 (2C); 28.24; 26.77; 22.62; 14.07. **HRMS**: $C_{14}H_{17}Br_2NO_3$: calculated: 407.9628; found: 407.9625.

[00135] ***Synthesis of 5-(octyl)-selenopheno[3,4-c]pyrrole-4,6-dione (13)***: *n*-Octylamine (0.114 g, 0.88 mmol) was added to selenophene-3,4-dicarboxylic acid **(12)** (0.175 g, 0.80 mmol). The reaction mixture was stirred and heated to 200°C over a period of 40 minutes. The mixture was then reacted at 200°C for an additional 20 min, cooled down, diluted with dichloromethane (20 mL) and concentrated under reduced pressure. The crude solid product was purified by column chromatography using dichloromethane as the eluent to afford 0.23g (Y = 84%) of a beige solid. **m.p.** 107-108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 8.62 (s, 2H); 3.59 (t, 2H, *J* = 7.3 Hz); 1.67-1.60 (m, 2H); 1.31-1.25 (m, 10H); 0.87 (t, 3H, *J* = 6.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ: 163.15; 138.59; 132.15; 38.59; 31.78; 29.17 (2C); 28.38; 26.89; 22.63; 14.09. **HRMS**: $C_{14}H_{19}N_1O_2Se_1$: calculated: 313.0589; found: 313.0589.

[00136] ***Synthesis of 1,3-dibromo-5-(octyl)-selenopheno[3,4-c]pyrrole-4,6-dione (14)***: 5-Octyl-selenopheno[3,4-*c*]pyrrole-4,6-dione **(13)** (0.050 g, 0.16 mmol) **(13)** was dissolved in sulfuric acid (0.20 mL) and trifluoroacetic acid (0.65 mL). The reaction mixture was stirred in the dark and N-bromosuccinimide (0.090 g, 0.50 mmol) was subsequently added in small portions. The mixture was stirred overnight at room temperature. Cold water (2 mL) was then added and the resulting mixture was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography

using ethyl acetate/hexanes (1:9) as the eluent to afford 0.06g (Y = 80%) as an orange solid. **m.p.** 129-130°C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 3.57 (t, 2H, *J* = 7.3 Hz); 1.67-1.60 (m, 2H); 1.31-1.26 (m, 10H); 0.87 (t, 3H, *J* = 6.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 161.18; 136.69; 118.28; 39.08; 32.01; 29.34(2C); 28.39; 27.05; 22.86; 14.32. **HRMS**: $C_{14}H_{17}Br_2N_1O_2Se_1$: calculated: 468.8791; found: 468.8791.

[00137] ***General Procedure for Stille Cross-Coupling Polymerization***: Distannate co-monomers **(15** or **16)** (0.1 mmol) and dibromo co-monomers **(3a-c**, **11**, or **14)** (0.1 mmol), $Pd_2(dba)_3$ (2 mol %) and P(*o*-Tolyl)$_3$ or $AsPh_3$ (8 mol %) were put in microwave vial (2-5 mL). The vial was carefully sealed and purged three times by vacuum/argon cycling. The solids were dissolved in 5 mL of dry and oxygen free toluene. The mixture was heated to 110°C using an oil bath equipped with a temperature controller. After 72h, bromobenzene was added to the viscous reaction mixture and reacted for an additional hour. Trimethyltin phenyl was then added and reacted for 1h to complete the end capping procedure. The whole mixture was cooled to room temperature and poured into methanol and the solid recovered by filtration. The polymers were purified by Soxhlet extraction using acetone and then hexane. The polymers were then extracted with chloroform. The solvent was reduced to about 10-15 mL and the mixture was poured into cold methanol. Polymers were recovered by filtration.

[00138] ***General Procedure for Direct Heteroarylation Polymerization***: Dibromo co-monomers **(17 - 20)** (0.1 mmol), 5-alkyl-thieno[3,4-c]pyrrole-4,6-dione **(2a,b)** or 5-alkyl-furo[3,4-*c*]pyrrole-4,6-dione **(7a-c)** (0.1 mmol), *trans*-di(μ-acetato)-bis[*o* -(di-*o*-tolyl-phosphino)benzyl]dipalladium(II) (4% mol), tris-(*o*-methoxyphenyl)phosphine (8% mol), Cs_2CO_3 (2 eq.) and pivalic acid (30% mol) were put in microwave vial (2-5 mL). The vial was carefully sealed and put under vacuum for 1h. The solids were dissolved in dry and oxygen free toluene. The system was purged three times by vacuum/argon cycling. The mixture was heated to 120°C using an oil bath equipped with a temperature controller. After 24-36 h, the polymer was end-capped. The whole mixture was cooled to room temperature and poured into methanol and the resulting solid was recovered by

filtration. The polymers were purified by Soxhlet extraction using acetone and then hexane. The polymers were then extracted with chloroform. The solvent was reduced to about 10-15 mL and the mixture was poured into cold methanol. Polymers were recovered by filtration.

[00139] While the present disclosure has been described with reference to what are presently considered to be the preferred examples, it is to be understood that the disclosure is not limited to the disclosed examples. To the contrary, the disclosure is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

[00140] All publications, patents and patent applications are herein incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

REFERENCES REFERRED TO IN THE SPECIFICATION

1. Coakley, K. M.; McGehee, M. D. *Chem. Matter.* **2004**, *16*, 4533.
2. Hoppe, H.; Sariciftci, N. S. *J. Mater. Chem.* **2006**, *16*, 45.
3. Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.
4. Brabec, C. J.; Dyakonov, V.; Scherf, U. In *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*; (Eds: J. Wiley & Sons), **2008**.
5. Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394.
6. Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323.
7. Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. *Adv. Mater.* **2010**, *22*, 3839.
8. Gendron, D.; Leclerc, M. *Energy Environ. Sci.* **2011**, *4*, 1225.
9. Boudreault, P.-L. T.; Najari, A.; Leclerc, M. *Chem. Mater.* **2011**, *23*, 456.
10. Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nature Mater.* **2007**, *6*, 497.
11. Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nature Photon.* **2009**, *3*, 297.
12. Sun, Y.; Takacs, C. J.; Cowan, S. R.; Seo, J. H.; Gong, X.; Roy, A.; Heeger, A. J. *Adv. Mater.* **2011**, *23*, 2226.
13. Uy, R. L.; Price, S. C.; You, W.; *Macromol. Rapid Commun.* **2012**, *33*, 1162.
14. Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Aïch, B. R.; Tao, Y.; Leclerc, M.; *J. Am. Chem. Soc.* **2010**, *132*, 5330.
15. Piliego, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 7595.
16. Najari, A.; Beaupré, S.; Berrouard, P.; Zou, Y.; Pouliot, J.-R.; Lepage-Pérusse, C.; Leclerc, M. *Adv. Funct. Mater.* **2011**, *21*, 718.
17. Chu, T.-Y.; Liu, J.; Beaupré, S.; Zang, Y.; Pouliot, J.-R.; Wakim, S.; Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250.
18. Su, M.-S.; Kuo, C.-Y.; Yuan, M.-C.; Jeng, U.; Su, C.-J.; Wei, K.-H. *Adv. Mater.* **2011**, *23*, 3315.
19. Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 10062.
20. Small, C. E.; Chen, S.; Subbiah, J.; Amb, C. M.; Tsang, S.-W.; Lai, T.-H.; Reynolds, J. R.; So, F. *Nature Photon.* **2012**, *6*, 115.
21. Lu, J.; Chu, T.-Y.; Beaupré, S.; Zhang, Y.; Pouliot, J.-R.; Zhou, J.; Najari, A.; Leclerc, M.; Tao, Y. *Adv. Funct. Mater.* **2012**, *22*, 2345.
22. Aïch, B. R.; Lu, J.; Beaupré, S.; Leclerc, M.; Tao, Y. *Org. Electron.* **2012**, *13*, 1736.

23. Jo, J.; Pron, A.; Berrouard, P.; Leong, W. L.; Yuen, J. D.; Moon, J. S.; Leclerc, M.; Heeger, A. J. *Adv. Energy Mater.* **2012**, doi: 10.1002/aenm.201200350.

24. Najari, A.; Berrouard, P.; Ottone, C.; Boivin, M.; Zou, Y.; Gendron, D.; Caron, W.-O.; Legros, P.; Allen, C. N.; Sadki, S.; Leclerc, M. *Macromolecules* **2012**, *45*, 1833.

25. Wen, S.; Cheng, W.; Li, P.; Yao, S.; Xu, B.; Li, H.; Gao, Y.; Wang, Z.; Tian, W. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, doi: 10.1002/pola.26164.

26. Guo, X.; Ortiz, R. P.; Zheng, Y.; Kim, M.-G.; Zhang, S.; Hu, Y.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 13685.

27. Guo, X.; Xin, H.; Kim, F. S.; Liyanage, A. D. T.; Jenekhe, S. A.; Watson, M. D. *Macromolecules* **2011**, *44*, 269.

28. Zhang, Y.; Zou, J.; Yip, H.-L.; Sun, Y. S.; Davies, J. A.; Chen, K.-S.; Acton, O.; Jen, A. K.-Y. *J. Mater. Chem.* **2011**, *21*, 3895.

29. MacNeill, C. M.; Peterson, E. D.; Noftle, R. E.; Carroll, D. L.; Coffin, R. C. *Synth. Met.* **2011**, *161*, 1137.

30. Li, Z.; Tsang, S.-W.; Du, X.; Scoles, L.; Robertson, G.; Zhang, Y.; Toll, F.; Lu, J.; Ding, J. *Adv. Funct. Mater.* **2011**, *21*, 3331.

31. Hong, Y.-R.; Wong, H.-K.; Moh, L. C. H.; Tan, H.-S.; Chen, Z.-K. *Chem. Commun.* **2011**, *47*, 4920.

32. Yuan, M.-C.; Chou, Y.-J.; Chen, C.-M.; Hsu, C.-L.; Wei, K.-H. *Polymer* **2011**, *52*, 2792.

33. Gendron, D.; Morin, P.-O.; Berrouard, P.; Allard, N.; Aïch, B. R.; Garon, C. N.; Tao, Y.; Leclerc, M. *Macromolecules* **2011**, *44*, 7188.

34. Zhang, G.; Fu, Y.; Zhang, Q.; Xie, Z. *Chem. Commun.* **2011**, *46*, 4997.

35. Berrouard, P.; Najari, A.; Pron, A. ; Gendron, D.; Morin, P.-O.; Pouliot, J.-R.; Veilleux, J.; Leclerc, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 2068.

36. Politis, J. K.; Nemes, J. C.; Curtis, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 2537.

37. Bunz, U. H. F. *Angew. Chem. Int. Ed.* **2010**, *49*. 5037.

38. Gidron, O.; Diskin-Posner, V.; Bendikov, M. *J. Am. Chem. Soc.* **2010**, *132*, 2148.

39. Heeney, M.; Zhang, W.; Crouch, D. J.; Chabinyc, M. L.; Gordeyev, S. ; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, 5061.

40. Ballantyne, A. M.; Chen, L.; Nelson, J.; Bradley, D. D. C.; Astuti, Y.; Maurano, A.; Shuttle, C. G.; Durrant, J. R.; Heeney, M.; Duffy, W.; McCulloch, I. *Adv. Mater.* **2007**, *19*, 4544.

41. Haid, S.; Mishra, A.; Uhrich, C.; Pfeiffer, M.; Bäuerle, P. *Chem. Mater.* **2011**, *23*, 4435.

42. Dang, M. T.; Hirsh, L.; Wantz, G. *Adv. Mater.* **2011**, *23*, 3597.

43. Devys, M.; Barbier, M.; Parisot, D. *Heterocycles* **1990**, *31*, 1485.

44. Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

45. Nakayama, K.; Harigaya, Y.; Okamoto, H.; Tanaka, A. *J. Heterocyclic Chem.* **1991**, *28*, 853.

46. Paulmier, C.; Morel, J.; Pastour, P. *Bull. Soc. Chim. Fr.* **1969**, 2511.

47. P. Berrouard, S. Dufresne, A. Pron, J. Veilleux, M. Leclerc, *J. Org. Chem.*, **2012**.

48. Oosterhout, S. D.; Wienk, M. M.; Al-Hashimi, M.; Heeney, M.; Janssen, R. A. J. *J. Phys. Chem. C* **2011**, *115*, 18901.

49. He, Y.; Zhou, Y.; Zhao, G.; Min, J.; Guo, X.; Zhang, B.; Zhang, M.; Zhang, J.; Li, Y.; Zhang, F.; Inganäs, O. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 1822.

50. Ku, S.-Y.; Liman, C. D.; Burke, D. J.; Treat, N. D.; Cochran, J. E.; Amir, E.; Perez, L. A.; Chabinyc, M. L.; Hawker, C. J. *Macromolecules* **2011**, *44*, 9533.

Table 1: M_n, M_w and PDI data for Various Polymers

Polymer	Yield (%)	M_n[a] (kDa)	M_w[a] (kDa)	PDI[a]
P1[S]	98	20	47	2.4
P1[H]	65	51	145	2.9
P2[S]	95	11	21	1.9
P2[H]	78	18	39	2.2
P3[S]	93	13	30	2.3
P4[S]	84	12	17	1.4
P4[H]	38	18	28	1.6
P5[H]	62	15	27	1.7
P6[H]	49	10	14	1.4
P7[H]	79	16	27	1.7
P8[H]	94	41	95	2.3
P9[H]	83	21	55	2.6
P10[H]	83	14	25	1.8
P11[H]	51	17	27	1.6

[a] determined by SEC in hot TCB (110 °C) using polystyrene standard; [S] Stille cross-coupling polymerization; [H] Direct heteroarylation polymerization.

Table 2: Optical and Electronic Properties for Various Polymers

Polymer	Optical Properties				Electrochemical Properties		
	λ_{max} solution[a]	λ_{max} film[b]	λ_{onset} film	E_g^{opt}	HOMO	LUMO	E_g^{cv}
	nm	nm	nm	eV[c]	eV	eV	eV
P1^S	550, 610	550, 610	685	1.80	5.56	3.75	1.81
P1^H	550, 610	550, 610	685	1.80	5.56	3.75	1.81
P2^S	533, 581	533, 581	652	1.90	5.65	3.79	1.86
P2^H	538, 586	538, 586	645	1.92	5.65	3.79	1.86
P3^S	565, 635	565, 635	700	1.77	5.51	3.75	1.76
P4^S	468	556, 634	700	1.77	5.64	3.97	1.71
P4^H	468	568, 630	683	1.81	5.68	3.81	1.87
P5^H	500	550	640	1.94	5.76	3.81	1.95
P6^H	477	580, 632	691	1.80	5.56	3.73	1.83
P7^H	550, 600	550, 600	657	1.89	5.54	3.75	1.79
P8^H	483	562, 620	677	1.83	5.66	3.86	1.80
P9^H	500	550, 600	643	1.93	5.65	3.80	1.85
P10^H	530, 604	568, 622	685	1.81	5.64	3.83	1.81
P11^H	535, 582	535, 582	630	1.97	5.80	3.84	1.96

[a] Dissolved in $CHCl_3$ or *o*-DCB; [b] Spin coated films; [c] Calculated from the absorption edge wavelength of films; [S] Stille cross-coupling polymerization; [H] Direct heteroarylation polymerization.

Claims:

1. A photoactive copolymer comprising repeating units of Formula I

$$-[A^1\text{-}A^2]- \qquad \textbf{I}$$

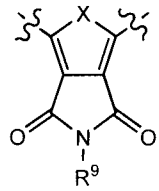
wherein:

A^1 is an electron donating unit; and

A^2 is an alkylfuro-[3,4-c]pyrrole-4,6-dione or an alkylselenopheno-[3,4-c]pyrrole-4,6-dione-derivative.

2. The photoactive copolymer of claim **1**, wherein A^1 is a mono or polycyclic heteroaryl that is unsubstitued or substituted with one or more $C_{1\text{-}20}$-alkyl or $C_{1\text{-}20}$-alkoxy.

3. The photoactive copolymer of any one of claims **1** to **2**, wherein A^2 is a monomer of Formula III:

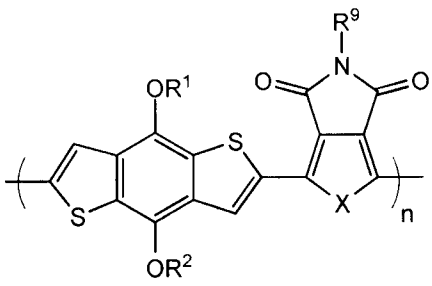


III

wherein X is selected from O and Se; and R^9 is selected from $C_{1\text{-}20}$-alkyl.

4. The photoactive copolymer of any one of claims **1** to **3**, comprising from 5 to 1000000 repeating units.

5. The photoactive copolymer of claim **3**, having the structure:



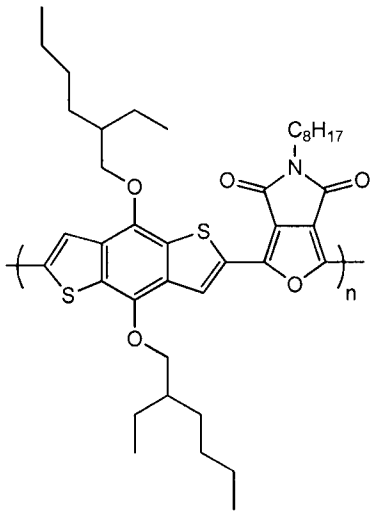
wherein:

R^1, R^2 and R^9 are independently selected from H and C_{1-20}-alkyl;

X is selected from O and Se; and

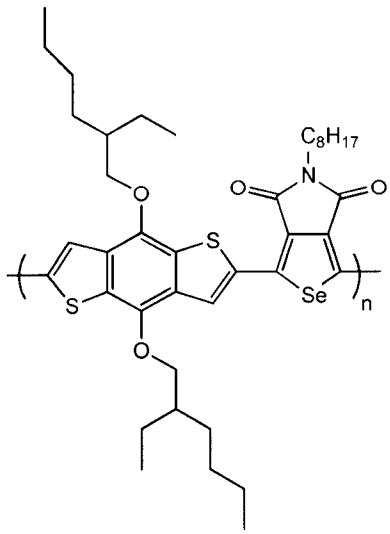
n is an integer ranging from 5 to 1000000.

6. The photoactive copolymer of claim **5**, having the structure:



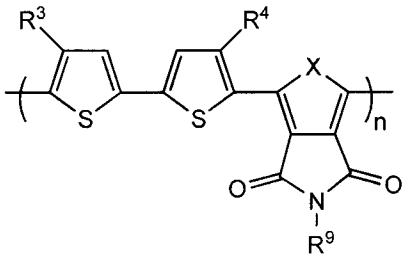
wherein n is an integer ranging from 5 to 1000000.

7. The photoactive copolymer of claim **5**, having the structure:



wherein n is an integer ranging from 5 to 1000000.

8. The photoactive copolymer of claim **3**, having the structure:



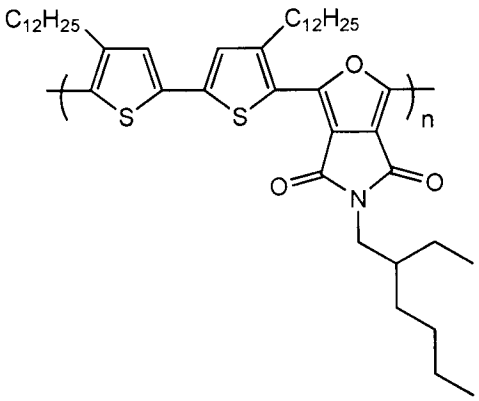
wherein:

R^3, R^4 and R^9 are independently selected from H and C_{1-20}-alkyl;

X is selected from O and Se; and

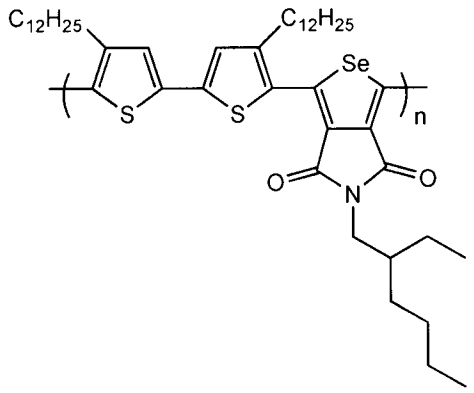
n is an integer ranging from 5 to 1000000.

9. The photoactive copolymer of claim **8**, having the structure:



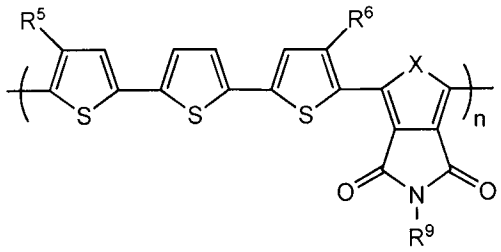
wherein n is an integer ranging from 5 to 1000000.

10. The photoactive copolymer of claim **8**, having the structure:



wherein n is an integer ranging from 5 to 1000000.

11. The photoactive copolymer of claim **3**, having the structure:



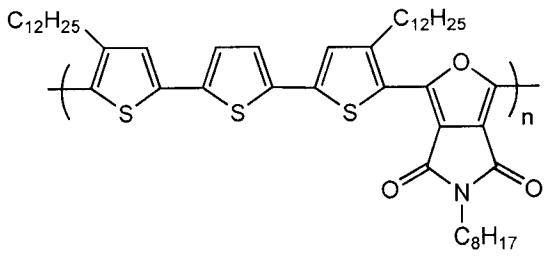
wherein:

R^5, R^6 and R^9 are independently selected from H and $C_{1\text{-}20}$-alkyl;

X is selected from O and Se; and

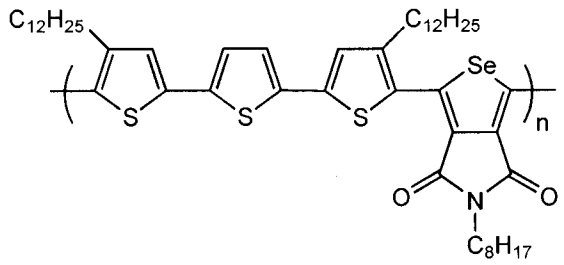
n is an integer ranging from 5 to 1000000.

12. The photoactive copolymer of claim **11**, having the structure:



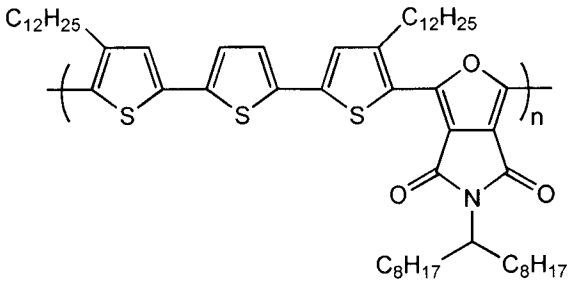
wherein n is an integer ranging from 5 to 1000000.

13. The photoactive copolymer of claim **11**, having the structure:



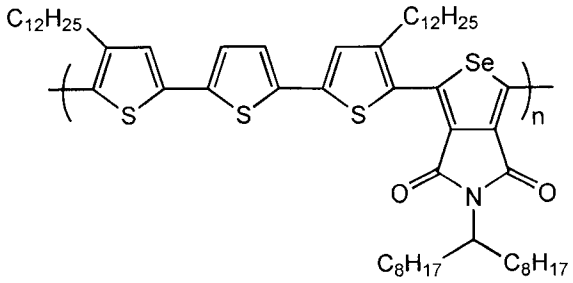
wherein n is an integer ranging from 5 to 1000000.

14. The photoactive copolymer of claim **11**, having the structure:



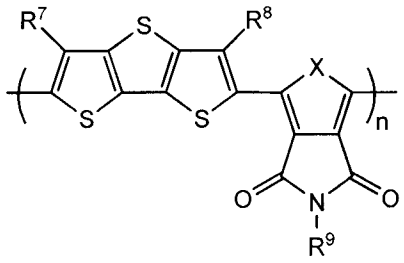
wherein n is an integer ranging from 5 to 1000000.

15. The photoactive copolymer of claim **11**, having the structure:



wherein n is an integer ranging from 5 to 1000000.

16. The photoactive copolymer of claim **3**, having the structure:



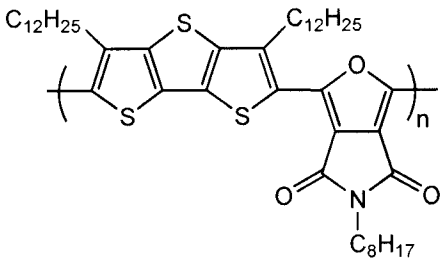
wherein:

R^7, R^8 and R^9 are independently selected from H and $C_{1\text{-}20}$-alkyl;

X is selected from O and Se; and

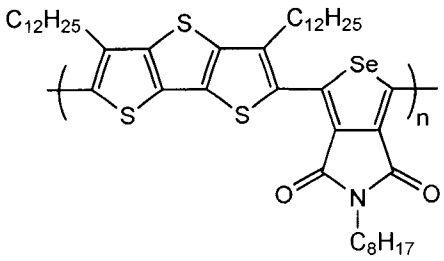
n is an integer ranging from 5 to 1000000.

17. The photoactive copolymer of claim **16**, having the structure:



wherein n is an integer ranging from 5 to 1000000.

18. The photoactive copolymer of claim **16**, having the structure:



wherein n is an integer ranging from 5 to 1000000.

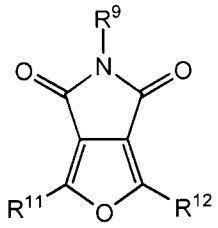
19. Use of the photoactive copolymer of any one of claims **1** to **18** in bulk heterojunction solar cells.

20. Use of the photoactive copolymer of any one of claims **1** to **18** in electronic devices.

21. The use of claim **20**, wherein the electronic devices include photovoltaic devices, OLEDs, OPVs, OFETs, transistors, batteries, printed electronics, sensors and sensors.

22. A co-monomer repeat unit comprising an alkylfuro-[3,4-c]pyrrole-4,6-dione-derivative or an alkylselenopheno-[3,4-c]pyrrole-4,6-dione-derivative.

23. The alkylfuro[3,4-c]pyrrole-4,6-dione derivative of claim **22**, having the structure:

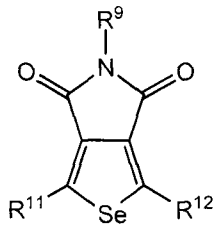


wherein R_9 is H or C_{1-20}-alkyl; and R^{11} and R^{12} are independently selected from H and halogen.

24. The alkylfuro[3,4-c]pyrrole-4,6-dione derivative of claim **23**, wherein R^9 is C_{1-20}-alkyl; and R^{11} and R^{12} are both hydrogen.

25. The alkylfuro[3,4-c]pyrrole-4,6-dione derivative of claim **23**, wherein R^9 is C_{1-20}-alkyl; and R^{11} and R^{12} are both Br.

26. The alkylselenopheno[3,4-c]pyrrole-4,6-dione derivative of claim **22**, having the structure:

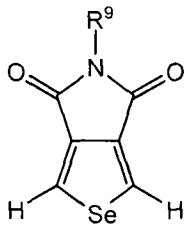


wherein R^9 is H or C_{1-20}-alkyl; and R^{11} and R^{12} are independently selected from H and halogen.

27. The alkylselenopheno [3,4-c]pyrrole-4,6-dione derivative of claim **26**, wherein R^9 is C_{1-20}-alkyl; and R^{11} and R^{12} are both hydrogen.

28. The alkylselenopheno [3,4-c]pyrrole-4,6-dione derivative of claim **26**, wherein R^9 is C_{1-20}-alkyl; and R^{11} and R^{12} are both Br.

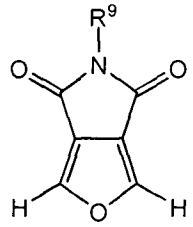
29. A process for preparing a selenopheno[3,4-c]pyrrole-4,6-dione derivative having the structure:



wherein R^9 is H or C_{1-20}-alkyl, the process comprising:

heating a reaction mixture comprising selenophene-3,4-dicarboxylic acid and an amine or alkylamine under conditions to provide the selenopheno[3,4-c]pyrrole-4,6-dione derivative.

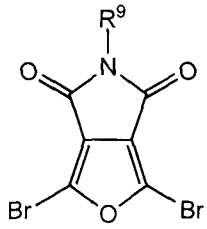
30. A process for preparing a furo[3,4-c]pyrrole-4,6-dione derivative having the structure:



wherein R^9 is H or C_{1-20}-alkyl, the process comprising:

reacting furo-3,4-dicarbonyl dichloride and an amine or an alkylamine under conditions to provide the furo[3,4-c]pyrrole-4,6-dione derivative.

31. A process for preparing a furo[3,4-c]pyrrole-4,6-dione derivative having the structure:



wherein R^9 is H or C_{1-20}-alkyl, the process comprising:

reacting 2,5-dibromo-furan-3,4-dicarbonyl dichloride and an amine or alkylamine under conditions to provide the alkylfuro[3,4-c]pyrrole-4,6-dione derivative.

32. A process for preparing furo-[3,4-c]pyrrole-4,6-dione-based or selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers, the process comprising:

reacting an activated furo-[3,4-c]pyrrole-4,6-dione or an activated selenopheno-[3,4-c]pyrrole-4,6-dione-derivative and a suitable electron donating moiety in the presence of one or more catalysts and one or more ligands under conditions for direct heteroarylation polymerization of the furo-[3,4-c]pyrrole-4,6-dione derivative or selenopheno-[3,4-c]pyrrole-4,6-dione-derivative and the electron donating moiety, to

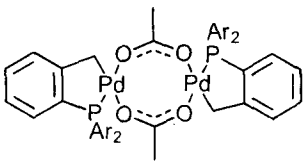
provide the furo-[3,4-c]pyrrole-4,6-dione-based or selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers.

33. The process of claim **32**, wherein electron donating moiety is a mono or polycyclic heteroaryl that is unsubstitued or substituted with one or more C_{1-20}-alkyl or C_{1-20}-alkoxy.

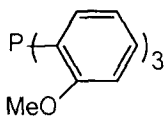
34. The process of claim **33**, further comprising, prior to isolating the furo-[3,4-c]pyrrole-4,6-dione-based or selenopheno-[3,4-c]pyrrole-4,6-dione-based copolymers, adding an end capping reagent.

35. The process of any one of claims **32** to **34**, wherein the one or more ligands are trialkyl or triaryl phosphines, in which the alkyl and aryl groups are substituted or unsubstituted, or the corresponding phosphonium salts, or complexes thereof with metals.

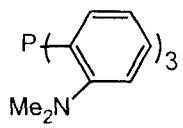
36. The process of claim **35**, wherein the one or more ligands are selected from: $P(t\text{-}Bu)_3HBF_4$, $P(Cy)_3HBF_4$, $P(t\text{-}Bu)_2MeHBF_4$, $P(o\text{-}tol)_3$, ,



Ar = o-tolyl



and



.

37. The process of any one of claims **32** to **36**, wherein the one or more catalysts are palladium (II) catalysts.

38. The process of claim **37**, wherein the palladium (II) catalyst is Pd(OAc)(o-Tol) or $Pd(OAc)_2$.

39. The process of any one of claims **32** to **38**, wherein the one or more catalysts are used in an amount of about 0.1 mol% to about 5 mol% based on the amount of monomers used.

40. The process of any one of claims **32** to **39**, wherein the one or more ligands are used in an amount of about 5 mol% to about 20 mol% based on the amount of monomers used.

41. The process of any one of claims **32** to **40**, further comprising adding one or more mild bases along with the activated furo-[3,4-c]pyrrole-4,6-dione-derivative or activated selenopheno-[3,4-c]pyrrole-4,6-dione-derivative, suitable electron donating moiety, one or more catalysts and one or more ligands under conditions for the direct heteroarylation of the activated furo-[3,4-c]pyrrole-4,6-dione-derivative or activated selenopheno-[3,4-c]pyrrole-4,6-dione-derivative and suitable electron donating moiety to provide the polymer.

42. An electronic device, comprising a photoactive copolymer as defined in any one of claims **1** to **18**.

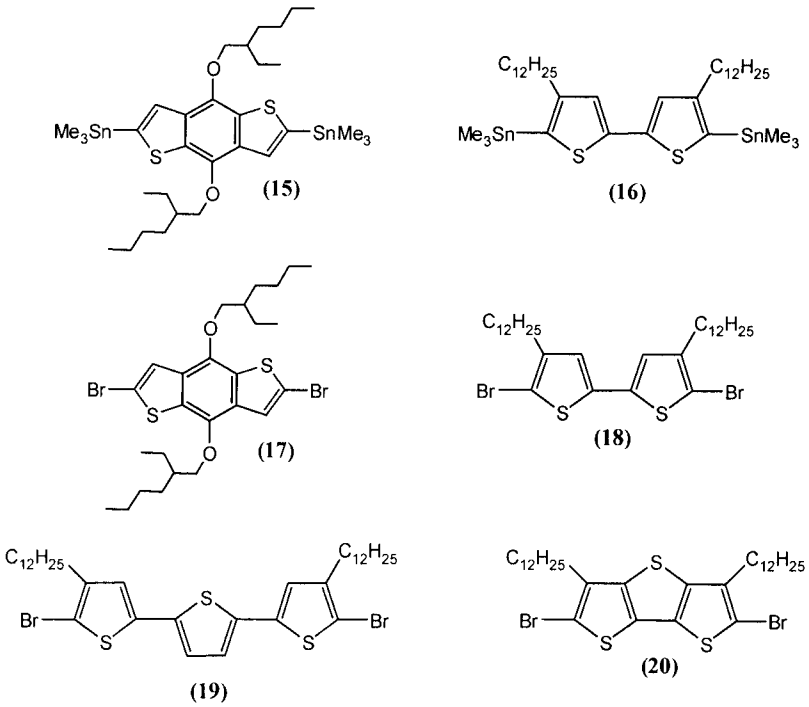

Me3Sn
SnMe3
(15)
C12H25
Me3Sn
SnMe3
(16)
Br
Br
(17)
C12H25
Br
Br
(18)
C12H25
Br
Br
(19)
C12H25
Br
Br
(20)

FIG. 1

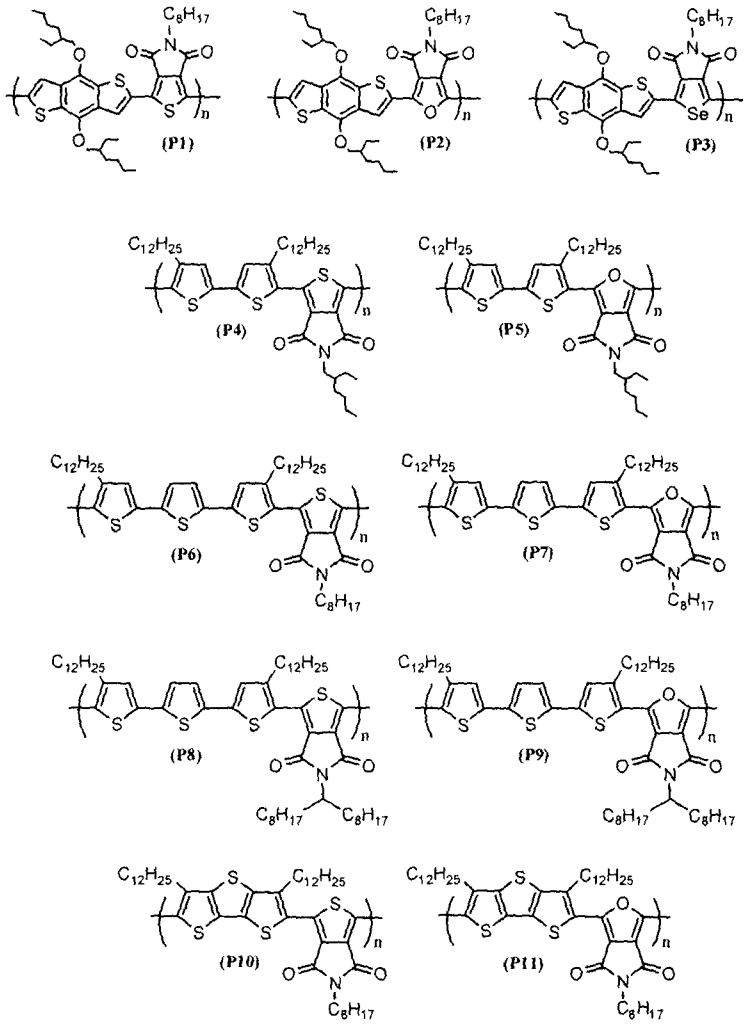
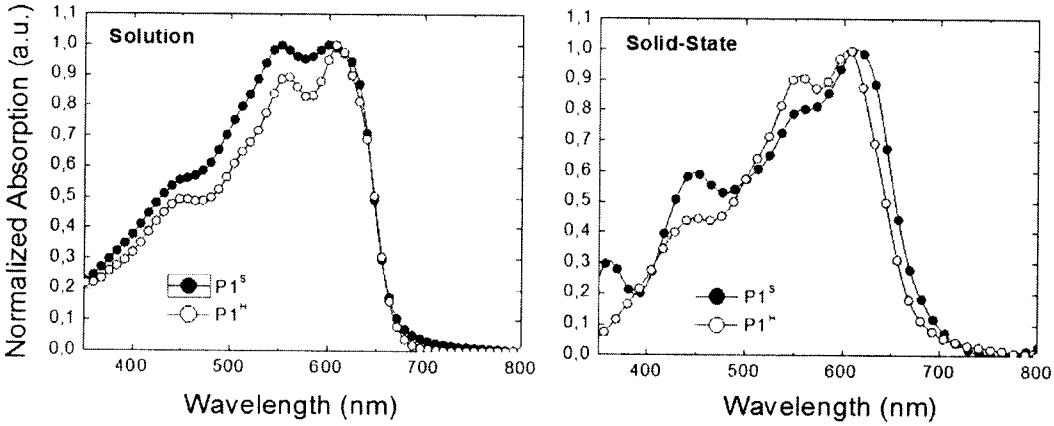
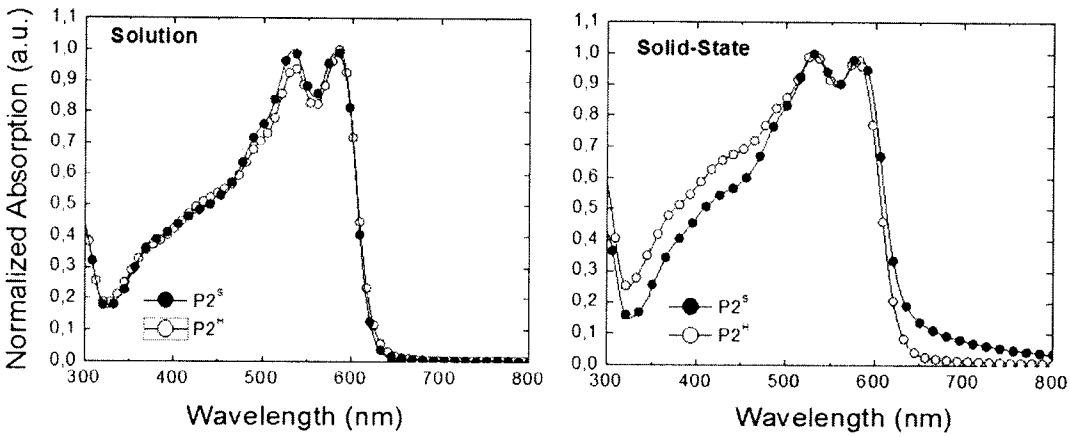


FIG. 2

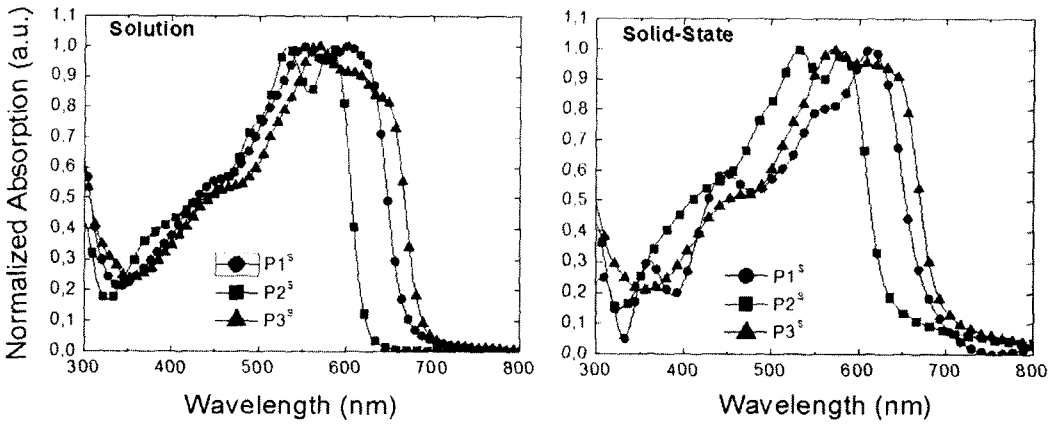

Solution
Solid-State
Normalized Absorption (a.u.)
Wavelength (nm)
P1S
P1M

(a)

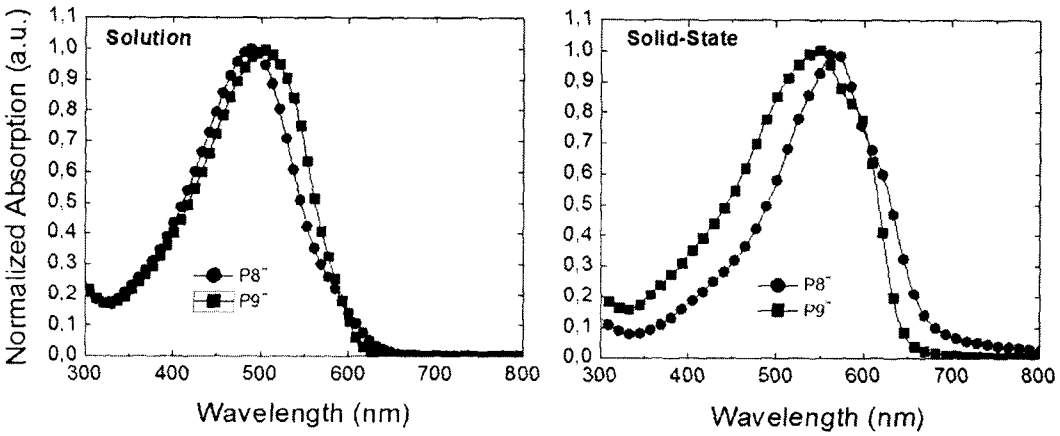

Solution
Solid-State
Normalized Absorption (a.u.)
Wavelength (nm)
P2S
P2M

(b)

FIG. 3


Solution
Solid-State
Normalized Absorption (a.u.)
Wavelength (nm)
P1S
P2S
P3S

(a)


Solution
Solid-State
Normalized Absorption (a.u.)
Wavelength (nm)
P8-
P9-

(b)

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/000736

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C07D 517/04*** (2006.01) , ***C07D 491/048*** (2006.01) , ***C08G 61/12*** (2006.01) , ***H01L 51/46*** (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)

C07D 517/04, C07D 491/048, C08G 61/12, H01L 51/*

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

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

STN, Canadian Patent Database, Scopus

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/127029 (MOON, J.-M. et al.) 23 October 2008 (23-10-2008) abstract, paragraphs [19], [22], [24] and [65], page 9	1-4, 8, 16, 19-22, 42
X	MARGETIC, D. et al.: "Domino Diels-Alder reactions of N-methoxyethyl-7-oxa-norbornadiene-2,3-dicarboximide: an elusive, highly reactive dienophile" *Tetrahedron*, Vol. 67(8), 2011, pages 1580-1588 5-Methyl-4H-furo[3,4-c]pyrrole-4,6-dione (CAS 1280113-42-9) i.e compound 6b	22-24
X	4H-furo[3,4-c]pyrrole-4,6-dione (CAS 877932-02-0)	22, 23

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 November 2013 (12-11-2013)	09 December 2013 (09-12-2013)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476

Authorized officer

Geneviève Fortier, PhD (819) 994-3433

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WARRENER, R. N. et al.: "Maleimide-fused cyclobutadienes and Dewar furans: trapping with dienes as a route to propellane photosubstrates with potential oxirene production" *Australian Journal of Chemistry*, Vol. 48(2), 1995, pages 241-260 1, 3, 5-trimethyl-4H-furo[3,4-c]pyrrole-4,6-dione (CAS 95641-45-5) i.e. compound 43	22
P, X	BEAUPRÉ, S. et al.: "Thieno-, Furo-, and Selenopheno[3,4-c]pyrrole-4,6-dione Copolymers: Effect of the Heteroatom on the Electrooptical Properties" *Macromolecules*, Vol. 45 (17), Published 28 August 2012, pages 6906-6914 the whole document	1-9, 11, 12, 14, 16, 17, 19-42
P, X	MERCIER, L. G. et al.: "Direct heteroarylation of ß-protected dithienosilole and dithienogermole monomers with thieno[3,4-c]pyrrole-4,6-dione and furo[3,4-c]pyrrole-4,6-dione" *Polymer Chemistry*, Vol. 4(20), Published 17 January 2013, pages 5252-5260	1-4, 19-24, 32, 33, 35, 36-42
P, X	IKAI, T. et al.: "Synthesis of seleno[3,4-c]pyrrole-4,6-dione based polymers for polymer solar cells" *Synthetic Metals*, Vol. 162(17-18), Available online 24 August 2012, pages 1707-1712 the whole document	1-5, 7, 19-22, 26-29, 32, 33, 35-37, 39, 40, 42
P, X	JP-2013-023572 (SEIJI, A. et al.) 04 February 2013 (04-02-2013) English abstract; co-monomers 1C and 1B on page 12; compounds with a furo[3,4-c]pyrrole-4,6-dione skeleton on pages 14-16, 27-29 and 40; synthetic scheme on page 51	1-4, 19-25, 32, 33, 35-40
A	CA 2,781,791 (LECLERC, M. et al.) 03 June 2011 (03-06-2011) the whole document	1-42

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/000736

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2008127029A1	23 October 2008 (23-10-2008)	JP2010527327A	12 August 2010 (12-08-2010)
		JP5180287B2	10 April 2013 (10-04-2013)
		KR20080092754A	16 October 2008 (16-10-2008)
		KR101128943B1	27 March 2012 (27-03-2012)
		US2010099840A1	22 April 2010 (22-04-2010)
JP2013023572A	04 February 2013 (04-02-2013)	None	
CA2781791A1	03 June 2011 (03-06-2011)	EP2507287A1	10 October 2012 (10-10-2012)
		US2013048075A1	28 February 2013 (28-02-2013)
		WO2011063534A1	03 June 2011 (03-06-2011)