(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 2014/031733 A1

(51) International Patent Classification:
H01L 51/00 (2006.01)

(21) International Application Number:
PCT/US2013/055967

(22) International Filing Date:
21 August 2013 (21.08.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/692,180 22 August 2012 (22.08.2012) US

(71) Applicant: **UNIVERSITY OF WASHINGTON THROUGH ITS CENTER FOR COMMERCIALIZATION** [US/US]; 4311 11th Ave. NE, Suite 500, Seattle, Washington 98105-4608 (US).

(72) Inventors: **JENEKHE, Samson A.**; 7223 57th Ave., NE, Seattle, Washington 98115 (US). **SUBRAMANIYAN, Selvam**; 2700 NE 125th St., Apt. 302, Seattle, Washington 98125 (US). **KIM, Felix Sunjoo**; 7551 37th Ave. NE, Seattle, Washington 98115 (US). **REN, Guoqiang**; 13263 35th Ave. NE, Seattle, Washington 98125 (US).

(74) Agents: **HENSCHEL, Rouget F.** et al.; Foley & Lardner LLP, 3000 K Street, N.W., Suite 600, Washington, District of Columbia 20007-5143 (US).

(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).

[Continued on next page]

(54) Title: DIKETOPYRROLOPYRROLE POLYMERS FOR ELECTRONICS AND OPTOELECTRONICS

(57) Abstract: Provided here are diketopyrrolopyrrole-based polymers comprising electron accepting subunits such as thiazolothiazole, benzobisthiazole or benzobisoxazole rings, and electron donating subunits such as certain heterocyclic groups. The polymers are useful for manufacturing organic electronic devices, including transistors and solar cells. Methods for making the polymers and the electronic devices comprising the polymers are also described.

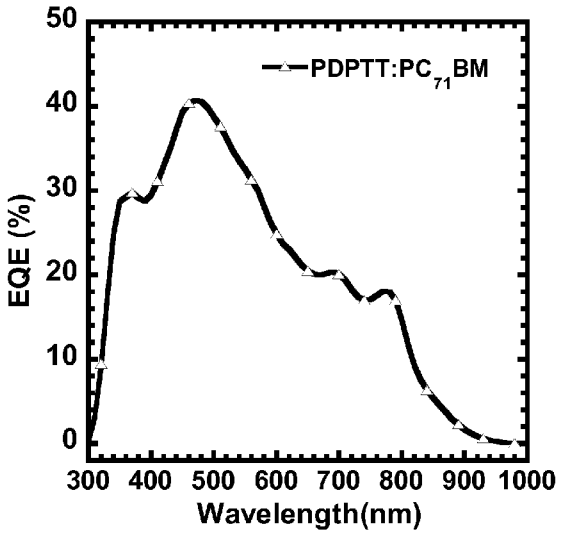


Figure 5

WO 2014/031733 A1

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

DIKETOPYRROLOPYRROLE POLYMERS FOR ELECTRONICS AND OPTOELECTRONICS

This invention was made with government support under DMR-0805259 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

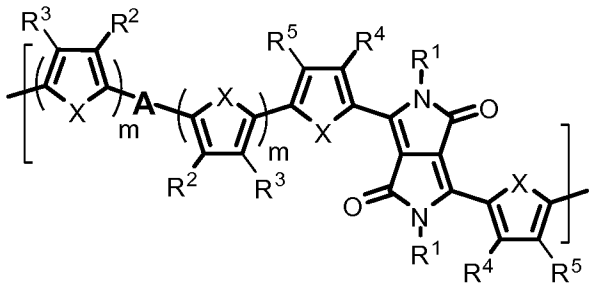
Solution-processable conjugated polymers are of growing interest for low-cost organic electronic devices including field-effect transistors and solar cells. Although progress has been made in developing high mobility p-type polymer semiconductors, device performance including carrier mobility, on/off current ratio and oxidative stability have not been satisfactory.

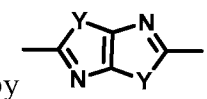
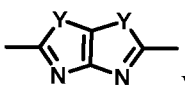
Thus, a need exists for developing new p-type polymer semiconductors that are suitable for use in high performance organic electronic devices including field-effect transistors and solar cells.

SUMMARY

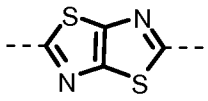
Embodiments described herein include compounds, compositions, devices, methods of making, and methods of using.

For example, provided is a polymer comprising a first repeating unit of formula (I)



(I); wherein: (i) X at each occurrence is independently selected from O, S and Se; (ii) m is 0, 1, 2 or 3; (iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group; (iv) the polymer has a Mw of 40,000 Da or more; and (v) A is an electron withdrawing group represented by  or,  wherein (a) Y at each occurrence is independently selected from O, S, Se and $N(R^6)$; and (b) R^6 is independently selected from hydrogen and optionally substituted C_1-C_{30}

linear, branched or cyclic organic group. The polymer can comprise other monomer units besides that shown in (I).

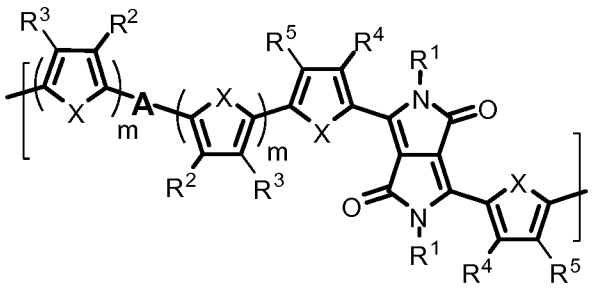
In one embodiment, A is represented by  .

In one embodiment, X is S. In one embodiment, m is 1.

In one embodiment, R^1 at each occurrence is independently selected from hydrogen, optionally substituted alkyl, optionally substituted heteroalkyl, fluoroalkyl, and fluoroheteroalkyl; and R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, optionally substituted alkyl, fluoroalkyl, optionally substituted alkoxy, fluoroalkoxy, optionally substituted thioalkyl, fluorothioalkyl, optionally substituted alkyl sulfoxide, fluoroalkyl sulfoxide, optionally substituted alkyl sulfone, and fluoroalkyl sulfone.

In another embodiment, R^1 at each occurrence is independently selected from C_4-C_{30} linear, branched or cyclic alkyl, and wherein R^2 at each occurrence is independently C_4-C_{30} linear or branched alkoxy.

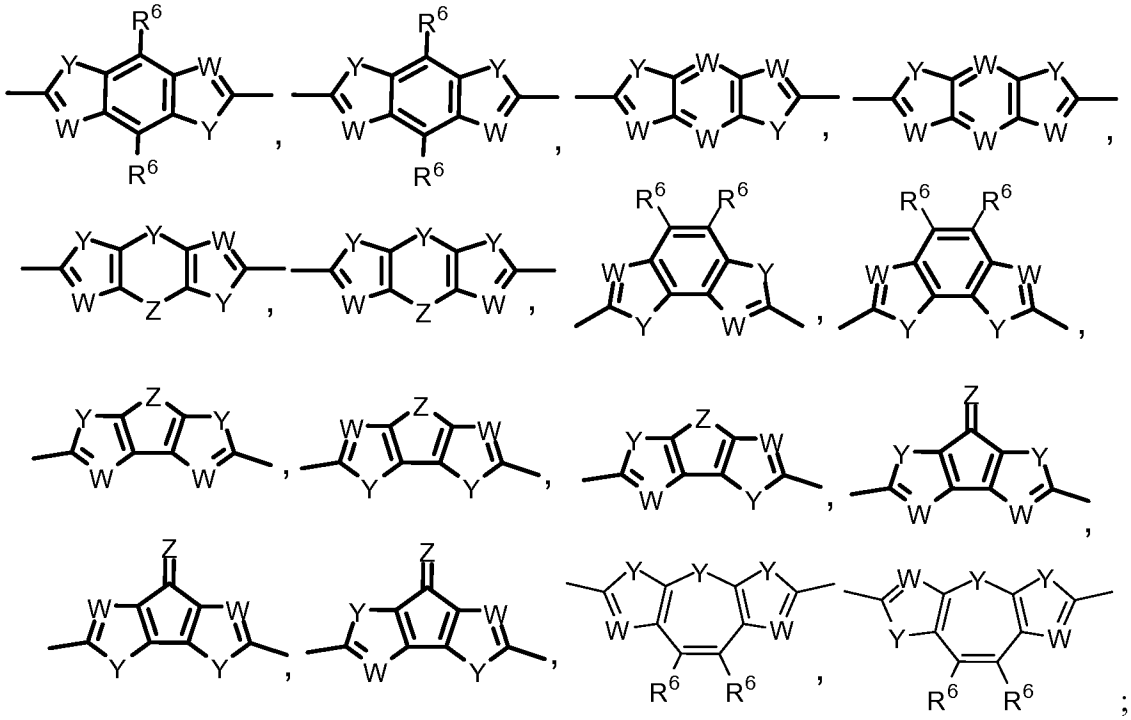
Also provided is a polymer comprising a first repeating unit of formula (I)



(I), wherein: (i) X at each occurrence is independently selected from O, S and Se; (ii) m is 0, 1, 2 or 3; (iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group; (iv) the polymer has a Mw of 40,000 Da or more; and (v) A is an electron withdrawing group comprising two or more rings fused together, with two of said rings each comprising at least one imine group.

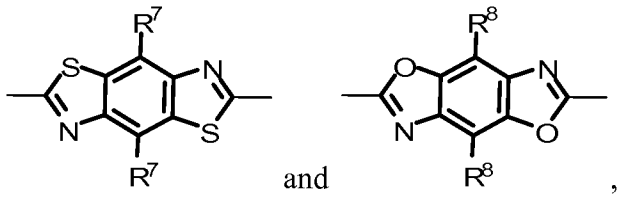
In one embodiment, A comprises at least two thiazole rings. In one embodiment, A comprises three or more rings fused together.

In one embodiment, A is selected from



wherein: (i) W at each occurrence is independently selected from N and $C(R^6)$; (ii) Y and Z at each occurrence is independently selected from O, S, Se, $P(R^6)$, $P(O)R^6$, $Si(R^6)_2$, $C(R^6)_2$ and $N(R^6)$; and (iii) R^6 at each occurrence is independently selected from hydrogen, halogen, hydroxyl, cyano, nitro, silyl, siloxanyl, and optionally substituted C_1-C_{30} linear, branched or cyclic organic group.

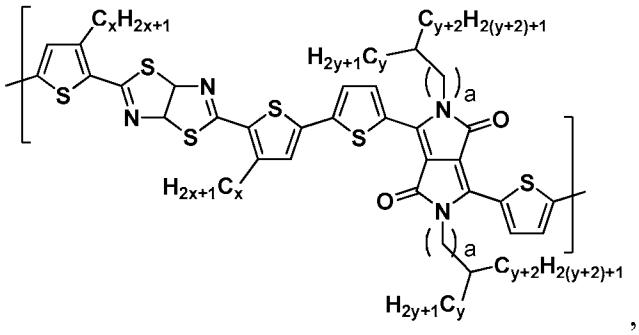
In one embodiment, wherein A is selected from



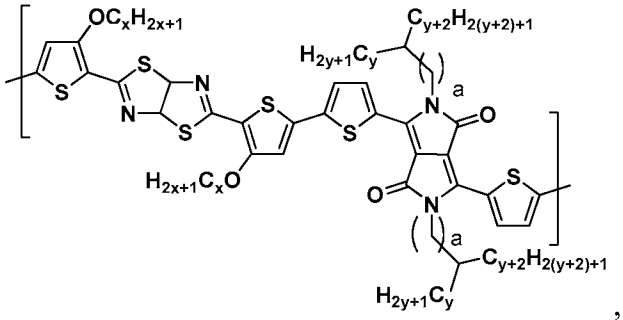
and

, wherein R^7 and R^8 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_4-C_{30} organic group.

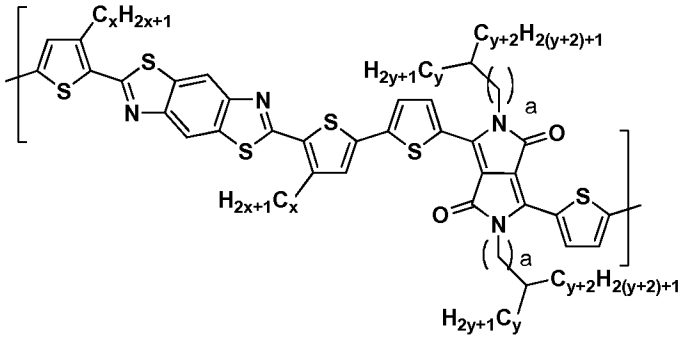
In one embodiment, the first repeating unit is selected from



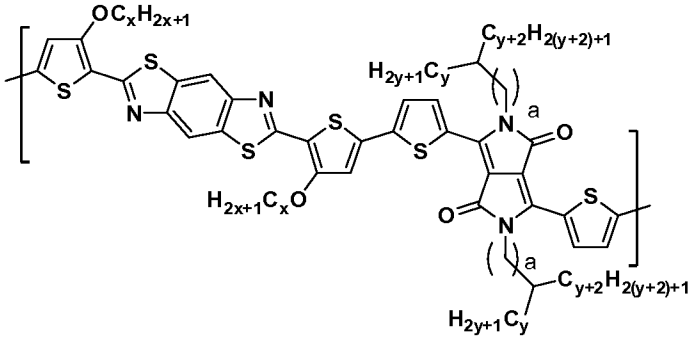
,



,

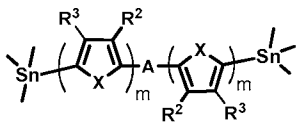
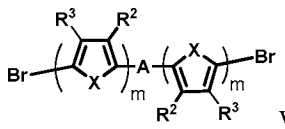
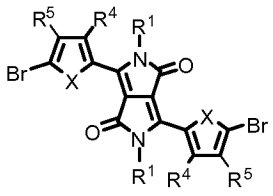
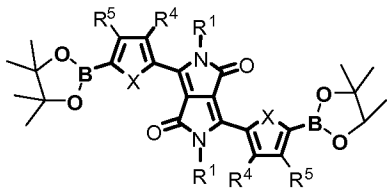


, and



, wherein x and y are 2-16, a is 1-15.

In one embodiment, the polymer consists essentially of the first repeating unit.

Further provided is a method for making the polymers described herein, comprising reacting a first compound represented by  or  with a second compound represented by  or  ; wherein: (i) X at each occurrence is independently selected from O, S and Se; (ii) m is 0, 1, 2 or 3; (iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group; and

(iv) A is an electron withdrawing group comprising two or more rings fused together, with two of said rings each comprising at least one imine group.

Additionally provided are compositions and electronic devices comprising the polymers described herein or made by the method described herein. In a particular embodiment, the electronic device is a field effect transistor having a charge carrier mobility of 0.3 cm^2/Vs or more.

At least one advantage for some embodiments of the donor-acceptor polymers described herein includes high carrier mobility.

At least another advantage for some embodiments of the donor-acceptor polymers described herein includes optimal HOMO/LUMO energy levels and more efficient hole injection.

At least another advantage for some embodiments of the donor-acceptor polymers described herein includes tunable band-gaps which can be optimized for particular applications.

At least a further advantage for some embodiments of the donor-acceptor polymers described herein includes high melting temperature, if a melting temperature is present.

At least a further advantage for some embodiments of the donor-acceptor polymers described herein includes high thermal, oxidative and mechanical stabilities.

At least an additional advantage for some embodiments of the donor-acceptor polymers described herein includes crystallinity and/or π-π stacking.

At least an additional advantage for some embodiments of the donor-acceptor polymers described herein includes good solubility in common organic solvents and good solution processability.

At least an additional advantage for some embodiments of the donor-acceptor polymer described herein includes that the polymer chains are self-assembled into nanowires having width of several nanometers and length of several nanometers to micrometers.

Other advantages for at least some embodiments include broad absorption bands (~500 nm to 900-1000 nm) and low optical band gaps (1.2-1.4 eV) for maximum light harvesting in solar cells.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows absorption spectra of PDPTT in $CHCl_3$ and as a thin film.

Figure 2 shows cyclic voltammogram of PDPTT film on a platinum electrode in 0.1 mole/L Bu_4NPF_6, CH_3CN solution. (a) Oxidation scans and (b) reduction scans.

Figure 3a and 3b show the electrical characteristics of PDPTT thin film transistors.

Figure 4 shows (a) The optical absorption spectrum of PDPTT:$PC_{71}BM$ blend films with the composition of 1:2, measured from solar cell devices, using ITO/PEDOT substrate as reference. (b) The current density — voltage characteristics of PDPTT:$PC_{71}BM$ solar cells with a structure of ITO/PEDOT/ PDPTT:$PC_{71}BM$/LiF/Al under dark and 100 mW/cm2 1.5AM sun illumination.

Figure 5 shows EQE spectra of PDPTT:PC71BM (1:2) solar cells.

Figure 6 shows TEM image of PDPTT:PC71BM thin film peeled from solar cells and their SAED patterns (1:2) are shown as inset.

Figure 7a and 7b show the electrical characteristics of PDPTTOx thin film transistors.

Figure 8 show TEM image of PDPTTOx:PC71BM thin film peeled from solar cells and their SAED patterns (1:2) are shown as inset.

DETAILED DESCRIPTION

INTRODUCTION

All references described herein are hereby incorporated by reference in their entireties. Various terms are further described herein below:

"A", "an", and "the" can refer to "at least one" or "one or more" unless specified otherwise.

"Optionally substituted" groups can refer to, for example, functional groups that may be substituted or unsubstituted by additional functional groups. For example, when a group is unsubstituted, it can be referred to as the group name such as, for example, alkyl or aryl. When a group is substituted with additional functional groups, it may more generically be referred to as substituted alkyl or substituted aryl (e.g., aralkyl).

"Alkyl" can refer to, for example, linear, branched, or cyclic alkyl groups. This term is exemplified by groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-pentyl, ethylhexyl, dodecyl, isopentyl, cyclohexyl, and the like.

"Aryl" can refer to, for example, aromatic carbocyclic groups having one or more single rings (e.g., phenyl or biphenyl) or multiple condensed rings (e.g., naphthyl or anthryl).

"Heteroalkyl" can refer to, for example, an alkyl group wherein one or more carbon atoms are substituted with heteroatoms.

"Heteroaryl" can refer to, for example, an aryl group wherein one or more carbon atoms are substituted with heteroatoms.

"Fluoroalkyl" can refer to, for example, an alkyl group wherein one or more hydrogen atoms are substituted with fluoro. Fluoroalkyl described herein include perfluoroalkyl as well as partially fluorinated alkyl.

"Fluoroalkoxide" can refer to, for example, an alkoxide group wherein one or more hydrogen atoms are substituted with fluoro. Fluoroalkoxide described herein include perfluoroalkoxide group as well as partially fluorinated alkoxide.

"Haloalkyl", "Haloalkenyl" and "Haloalkynyl" can refer to, for example, an alkyl, alkenyl group or alkynyl group wherein one or more hydrogen atoms are substituted with halogen.

"Silyl" can refer to, for example, a group of formula $-SiR'R''R'''$, wherein R', R'' and R''' are each independently a C_1-C_8 alkyl group.

"Siloxanyl" can refer to, for example, a group of formula $-O-SiR'R''R'''$, wherein R', R'' and R''' are each independently a C_1-C_8 alkyl group.

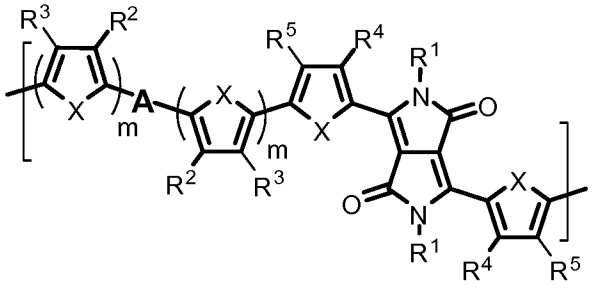
STRUCTURE OF THE DONOR-ACCEPTOR POLYMER

Many polymer semiconductors are known in the art and described in, for example, (i) Ha *et al.*, *J. Am. Chem. Soc.* 2011, 133, 10364-10367; (ii) Li *et al.*, *J. Mater. Chem.* 2011, 21, 10829-10835; (iii) Bronstein *et al.*, *J. Am. Chem. Soc.* 2011, 133, 3272-3275; (iv) Sonar *et al.*, *A. Energy Environ. Sci.* 2011, 4, 2288-2296; (v) Nelson *et al.*, *Adv. Mater.* 2010, 22, 4617-4621; (vi) Li *et al.*, *Adv. Mater.* 2010, 22, 4862-4866; (vii) Ha *et al.*, *Appl. Phys. Lett.* 2011, 98, 253305-3; (viii) Osaka *et al.*, *J. Am. Chem. Soc.* 2009, 131,2521-2529; (ix) Osaka *et al.*, *Adv. Mater.* 2007, 19, 4160-4165; (x) Ahmed *et al.*, *Macromolecules* 2010, 42, 8615-8618; (xi) Osaka *et al.*, *Adv. Mater.* 2010, 22, 4993-4997; (xii) Subramaniyan *et al.*, *Adv. Energy Mater.* 2011, 1, 854-860; (xiii) Subramaniyan *et al.*, *Macromolecules* 2011, 44, 6245-6248; and (xiv) Ahmed *et al.*, *Macromolecules* 2011, 44, 7207-7219; all of which are hereby incorporated by reference by their entireties.

Many embodiments described herein relate to a donor-acceptor polymer with a conjugated polymer backbone comprising at least one first repeating unit, said first repeating unit comprises at least one diketopyrrolopyrrole group, at least one electron accepting heteroaryl group comprising two or more imine (-C=N-) moieties, and at least two electron donating heteroaryl groups each comprising a five-membered heteroaromatic ring.

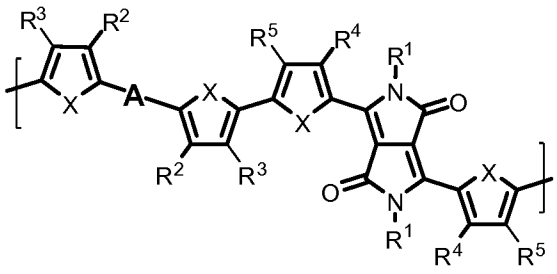
In some embodiments, the first repeating unit comprises a strong electron accepting diketopyrrolopyrrole group, a weak electron accepting group comprising at least two imine moieties, and at least two electron donating thiophene/furan/selenophene groups.

In some embodiments, the first repeating unit is represented by formula (I):



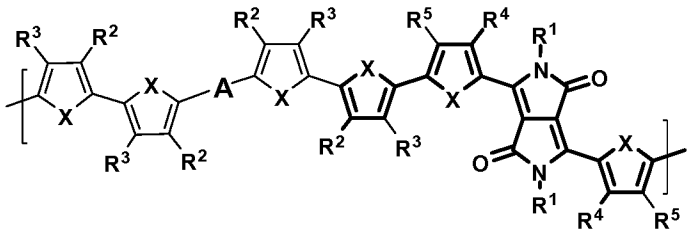
(I), wherein: (i) each X is independently selected from O, S and Se; (ii) m is 0, 1, 2 or 3; (iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group; and (iv) A is an electron withdrawing group comprising two or more imine moieties.

In some embodiments wherein m is 1, the first repeating unit can be represented by formula (II):



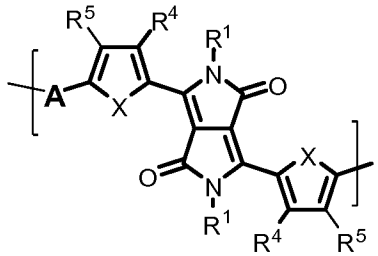
(II).

In some embodiments wherein m is 2, the first repeating unit can be represented by formula (III):



(III).

In some embodiments wherein m is 0, the first repeating unit can be represented by formula (IV):

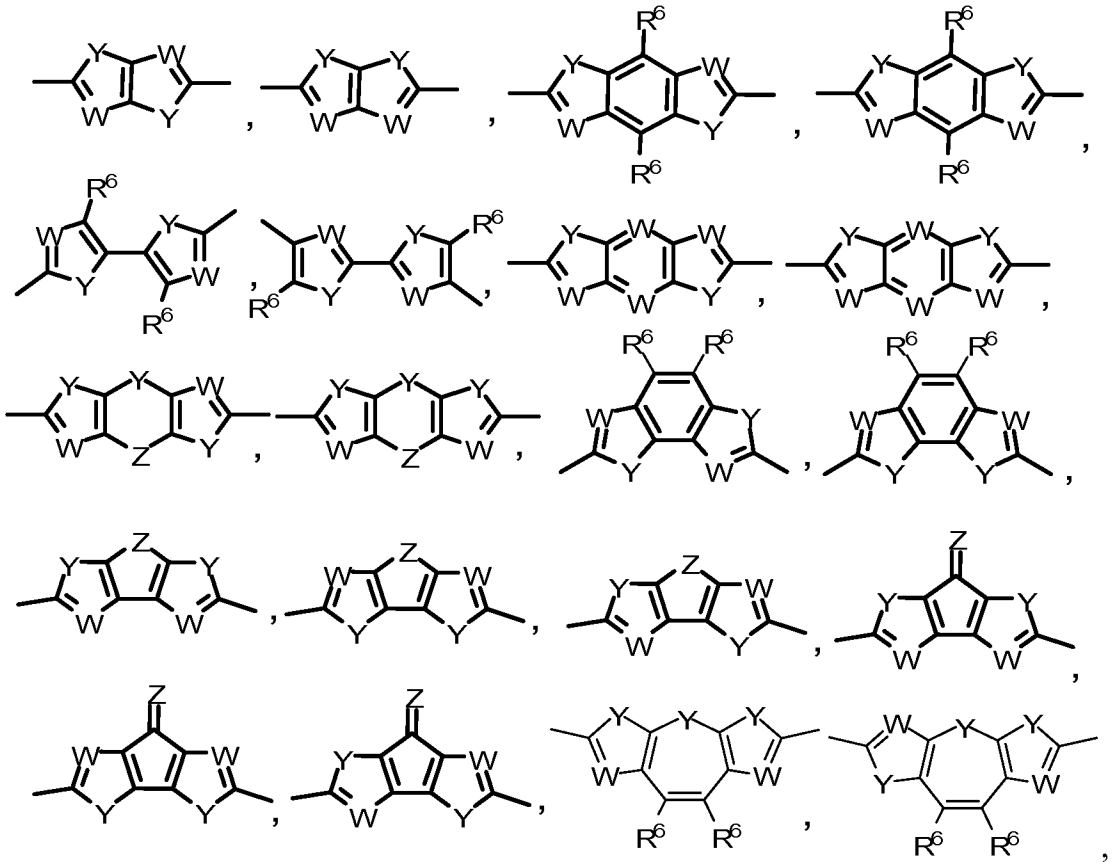


(IV).

In some embodiments, A is a heteroaryl group comprising two or more rings fused together, with two of said rings each comprising at least one imine group. In some embodiments, A comprises three or more rings fused together. In some embodiments, A

comprises at least two thiazole or oxazole rings fused together. In some embodiments, A comprises at least two thiazole or oxazole rings and a third ring fused together.

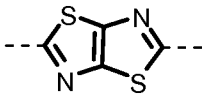
A can be selected from, for example, the following:

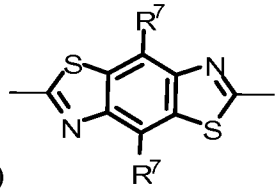


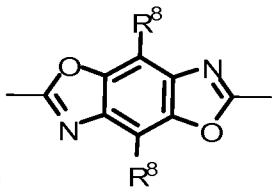
wherein: (i) each W is independently selected from N and C(R^6); (ii) each Y and Z is independently selected from O, S, Se, P(R^6), P(O)R^6, Si(R^6)$_2$, C(R^6)$_2$ and N(R^6); and (iii) each R^6 is independently selected from hydrogen, halogen, hydroxyl, cyano, nitro, silyl, siloxanyl, and an optionally substituted C_1-C_{30} linear, branched or cyclic organic group.

R^6 can be, for example, hydrogen, halogen, hydroxyl, cyano, nitro, silyl, siloxanyl, or an optionally substituted C_1-C_{30} organic group selected from alkyl, cycloalkyl, aralkyl, alkenyl, cycloalkenyl, alkynyl, mercapto, alkoxy, alkylthio, aryl, aryl ether, aryl thioether, heterocyclic, haloalkyl, haloalkenyl, haloalkynyl, aldehyde, carboxyl, ester, carbomyl or vinyl group.

R^6 can be, for example, hydrogen, a linear or branched C_1-C_{24}, C_1-C_{18} or C_1-C_{12} alkyl group, or a linear or branched C_1-C_{24}, C_1-C_{18} or C_1-C_{12} heteroalkyl group. R^6 can be, for example, hydrogen, a C_1-C_{24}, C_1-C_{18} or C_1-C_{12} linear or branched fluoroalkyl group, or a C_1-C_{24}, C_1-C_{18} or C_1-C_{12} linear or branched fluoroalkoxide group.

In some embodiment, A is a thiazolothiazole represented by  .

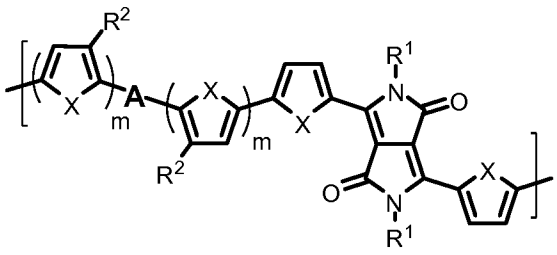
In another embodiment, A is an optionally substituted benzobisthiazole represented by (XXX)  , wherein each R^7 is independently selected from hydrogen, halogen, cyano, and optionally substituted C_4-C_{30} organic group. In one embodiment, each R^7 is a C_4-C_{30} linear or branched alkyl, alkoxide, fluoroalkyl or fluoroalkoxide. In one embodiment, A does not include the structure XXX.

In another embodiment, A is an optionally substituted benzobisoxazole represented by (XXXX)  , wherein each R^8 is independently selected from hydrogen, halogen, cyano, and optionally substituted C_4-C_{30} organic group. In one embodiment, each R^8 is a C_4-C_{30} linear or branched alkyl, alkoxide, fluoroalkyl or fluoroalkoxide. In one embodiment, A does not include the structure XXXX.

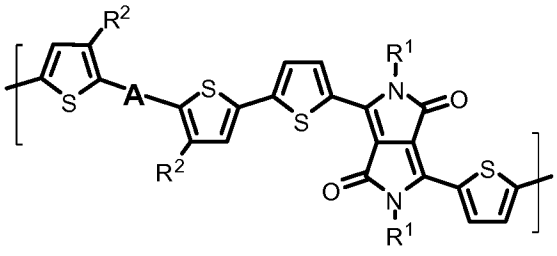
In some embodiments, X is S and the polymer comprises at least two, at least four, or at least six thiophene groups. In some embodiments, X is Se and the polymer comprises at least two, at least four or at least six selenophene groups. In some embodiments, X is O and the polymer comprises at least two, at least four or at least six furan groups.

R^1 can be independently selected from hydrogen, optionally substituted alkyl, optionally substituted heteroalkyl, fluoroalkyl, and fluoroheteroalkyl, R^2, R^3, R^4 and R^5 can be independently selected from, for example hydrogen, halogen, cyano, optionally substituted alkyl, fluoroalkyl, optionally substituted alkoxy, fluoroalkoxy, optionally substituted thioalkyl, fluorothioalkyl, optionally substituted alkyl sulfoxide, fluoroalkyl sulfoxide, optionally substituted alkyl sulfone, and fluoroalkyl sulfone,.

In some embodiments, R^3 and R^5 are hydrogen. In some embodiments, R^3, R^4 and R^5 are hydrogen, and the first repeating unit can be represented by formula (V):



(V). Further, wherein X is S and m is 1, the first repeating unit can be represented by formula (VI):

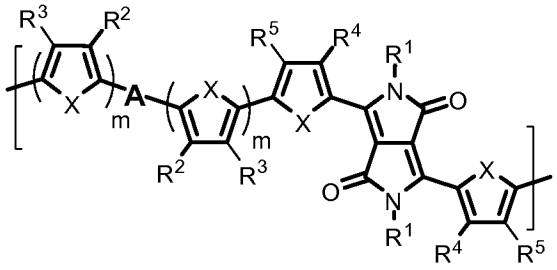


(VI).

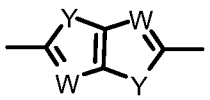
In some embodiments, R^1 and R^2 are independently selected from a linear or branched C_4-C_{24}, C_4-C_{18} or C_4-C_{12} alkyl group and a linear or branched C_4-C_{24}, C_4-C_{18} or C_4-C_{12} heteroalkyl group. In some embodiments, R^1 and R^2 are independently selected from a C_4-C_{24}, C_4-C_{18} or C_4-C_{12} linear or branched fluoroalkyl group and a C_4-C_{24}, C_4-C_{18} or C_4-C_{12} linear or branched fluoroalkoxide group.

In a particular embodiment, each R^1 is a C_4-C_{30} linear or branched alkyl, each R^2 is a C_4-C_{30} linear or branched heteroalkyl such as alkoxy, and each R^3, R^4 and R^5 is hydrogen.

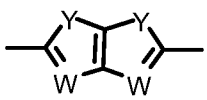
In a preferred embodiment, the donor-acceptor polymer comprises a first repeating unit of formula (I)



(I); wherein the polymer has a M_w of 40,000 Da or more; wherein A is an electron withdrawing group represented by

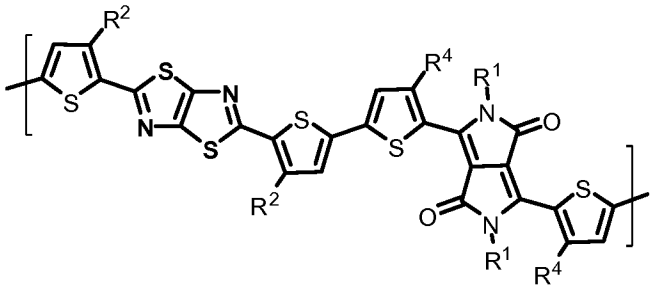


or



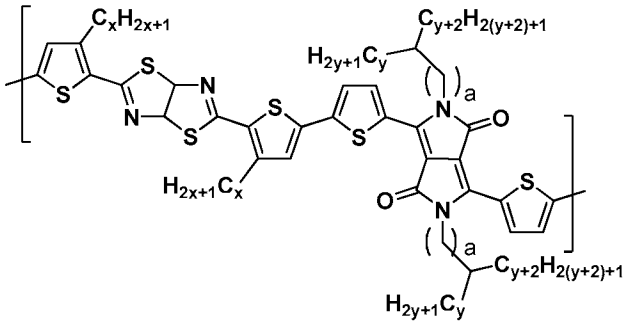
; and wherein X, Y, W, R^1, R^2, R^3, R^4, R^5 and m have the same definitions as previously described. In a more preferred embodiment, W is N and Y is selected from O, S, Se and N(R^6).

In a even more preferred embodiment, A is thiazolothiazole. Further, wherein X is S and m is 1, the first repeating unit can be represented by formula (VII):

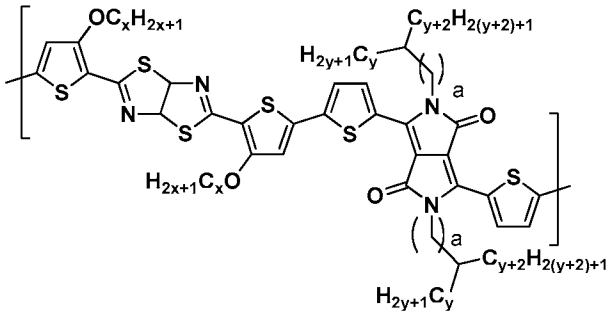


(VII). In an still more preferred embodiment, each R^1 and R^2 is a C_4-C_{30} linear or branched alkyl group or a C_4-C_{30} linear or branched heteroalkyl group such as alkoxy.

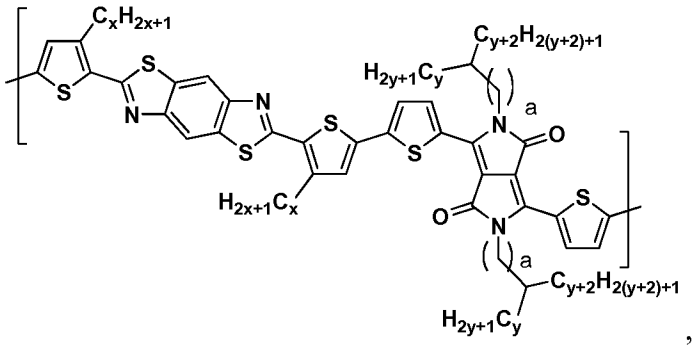
Particular embodiments of the first repeating units include the following:



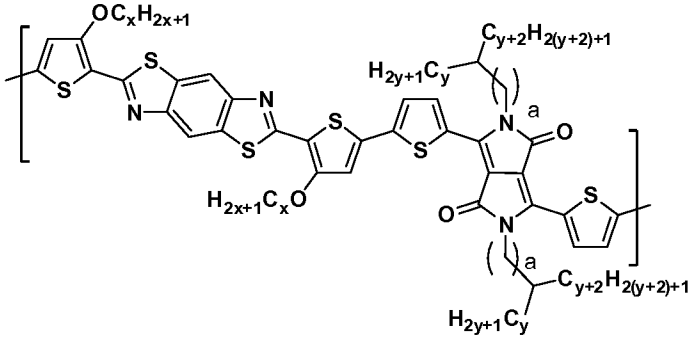
,



,



, and



, wherein x and y are 2-16, a is 1-15.

In some embodiments, the donor-acceptor polymer consists essentially of the first repeating unit. In other embodiments, the donor-acceptor polymer further comprises a second repeating unit and/or a third repeating unit different from the first repeating unit described herein. The second and third repeating units can be, for example, independently selected from electron-donating groups and electron-withdrawing groups known in the art.

The donor-acceptor polymer can be, for example, a homopolymer of the first repeating unit. The donor-acceptor polymer can also be, for example, a copolymer such as a block copolymer or an alternating copolymer. The molar percentage of the first repeating unit in the polymer can be, for example, at least 50%, or at least 70%, or at least 90%, or at least 95%, or at least 98%.

The donor-acceptor polymer described herein can have a weight-average molecule weight (M_w) of, for example, at least 30,000 Da, at least 40,000 Da, at least 50,000 Da, at least 60,000 Da, at least 80,000 Da, or at least 100,000 Da. The upper limit for M_w can be, for example, 250,000 Da or 1,000,000 Da. The donor-acceptor polymer described herein can have a number-average molecule weight (M_n) of, for example, at least 10,000 Da, at least 15,000 Da, at least 18,000 Da, at least 20,000 Da, or at least 30,000 Da. The upper limit for M_n can be, for example, 100,000 Da or 300,000 Da.

The donor-acceptor polymer described herein can have good solubility in common organic solvents such as chloroform, chlorobenzene, dichlorobenzene, etc. In some embodiments, the donor-acceptor polymer is soluble in chloroform, chlorobenzene and

dichlorobenzene at room temperature. The solubility of the donor-acceptor polymer in $CHCl_3$ at room temperature can be, for example, at least 10 mg/mL or at least 15 mg/mL, or at least 1 wt.% or at least 1.5 wt.%. The upper limit for said solubility in $CHCl_3$ at room temperature can be, for example, 100 mg/mL or 10 wt.%.

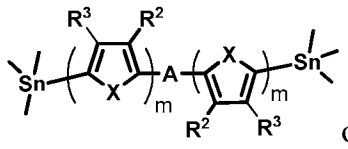
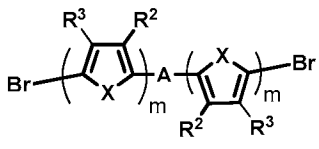
In many embodiments, as a result of the combinations of the diketopyrrolopyrrole group and "X" which is selected from S, or O and Se, the conjugated copolymers can have tunable "charge transfer", absorption bands in the UV or UV-visible or infra red region, HOMO/LUMO energy levels and charge carrier mobilities.

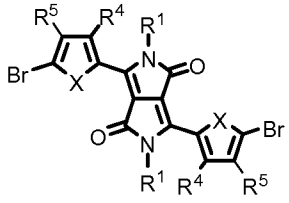
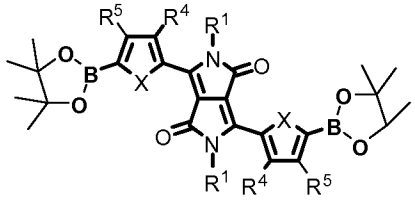
Further, in many embodiments, the electron deficient "A" group, which comprises two or more imine moieties in a fused polycyclic ring, can be conjugated with the neighboring heteroaromatic rings to impart electron donor characteristics such as low ionization potential or a low electrochemical oxidation potential on the conjugated polymer. *See, e.g.*, Shirota and Kageyama, *Chem. Rev.* **2007**, *107*, 953-1010; Parker, *J. Am. Chem. Soc.* **1976**, *98*, 98-103. Inclusion of the electron deficient "A" group in the diketopyrrolopyrrole-based donor-acceptor polymer permits fine tuning of the absorption bands, optical band-gaps, charge carrier mobilities, and oxidative and thermal stability of the copolymers.

It is also possible to "tune" the polymer by varying "X", "A", and any optional substituent to modulate the electronic and physical properties of the polymer in the solid state to encourage intermolecular π-stacking that promotes long range two or three dimensional order in the solid state, which promotes a high mobility of current carriers such as holes.

METHODS FOR MAKING THE DONOR-ACCEPTOR POLYMER

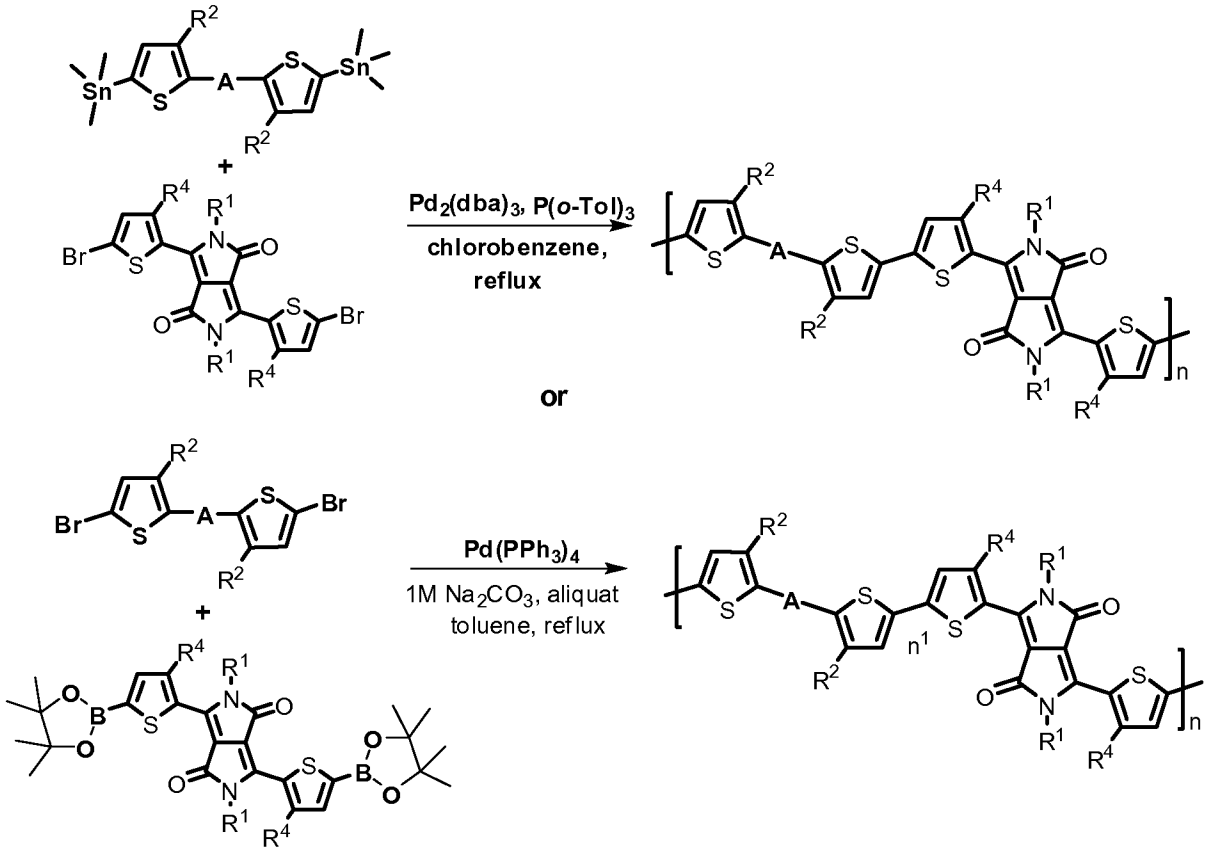
The donor-acceptor polymer described herein can be made by, for example, Stille coupling using di-tin monomers or Suzuki coupling using borate ester groups. Known catalysts including palladium complexes can be used.

In many embodiments, the polymer described herein can be made by reacting a first compound represented by  or  with a

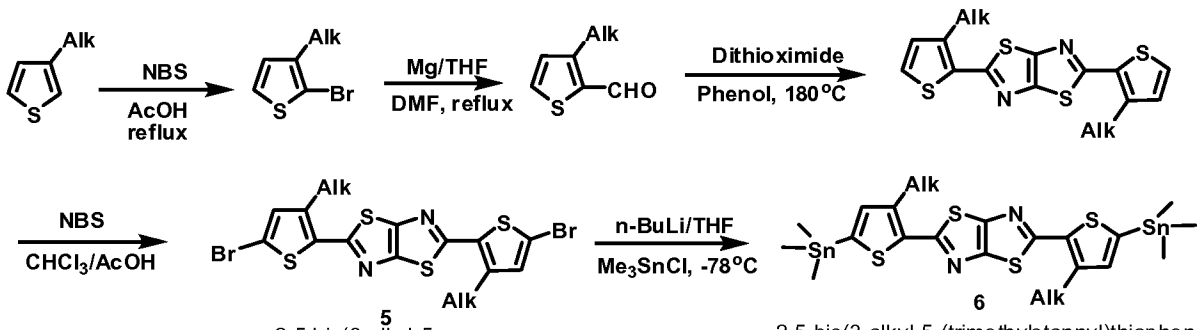
second compound represented by  or  ;

wherein A, X, R^1, R^2, R^3, R^4, R^5 and m have the same definitions as previously described.

Wherein X is S, and R^3 and R^5 are H, m is 1 the polymerization is illustrated in the scheme below.



Wherein R^2 is alkyl, X is S, m is 1 and A is thiazolothiazole, the first compound can be synthesized according to the following scheme.

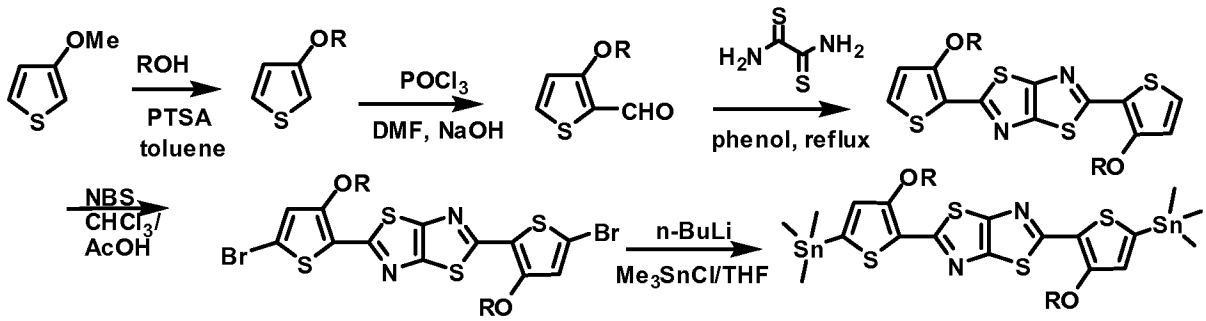


5
2,5-bis(3-alkyl-5-(tribromo)thiophen-2-yl) thiazolo[5,4-*d*]thiazole

6
2,5-bis(3-alkyl-5-(trimethylstannyl)thiophen-2-yl)thiazolo[5,4-*d*]thiazole

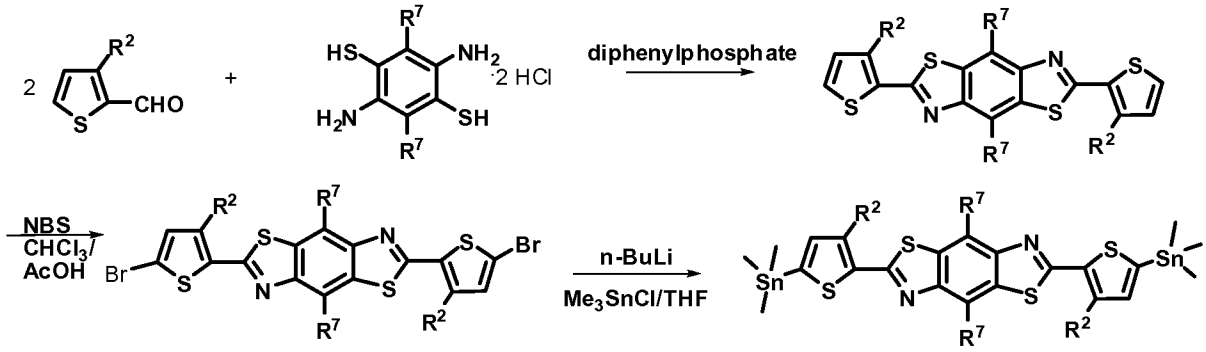
See Osaka, *et al J. Am. Chem. Soc.* 2009,*131*, 2521-2529.

Wherein R^2 is alkoxy, X is S, m is 1 and A is thiazolothiazole, the first compound can be synthesized according to the following scheme.



See Subramaniyan *et al Adv. Ener. Mater.* 2011, *1*, 854-860.

Wherein X is S, m is 1 and A is benzobisthiazole, the first compound can be synthesized according to the following scheme.

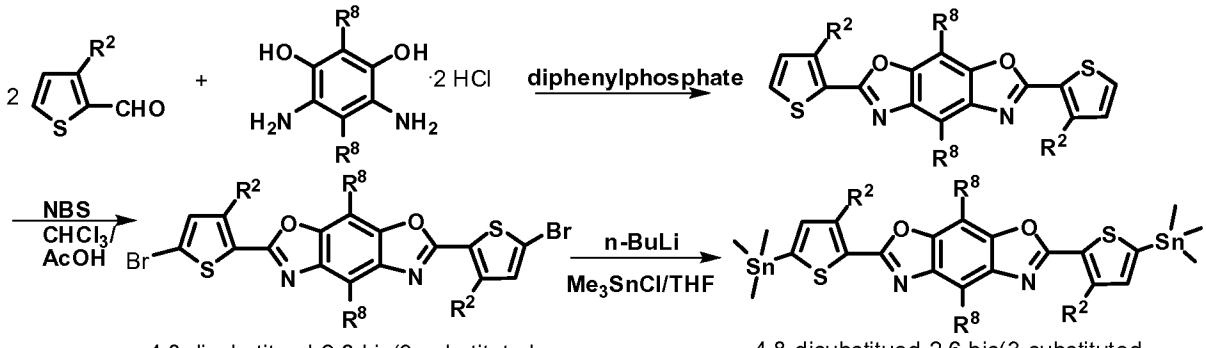


4,8-disubstitued-2,6-bis(3-substitutedl-5-(tribromo)thiophen-2-yl) benzo[1,2-*d*:4,5-*d'*]bis(thiazole)

4,8-disubstitued-2,6-bis(3-substitutedl-5-(trimethylstannyl)thiophen-2-yl) benzo[1,2-*d*:4,5-*d'*]bis(thiazole)

Ahmed *et al Macromolecules* 2011, *44*, 7207-7219

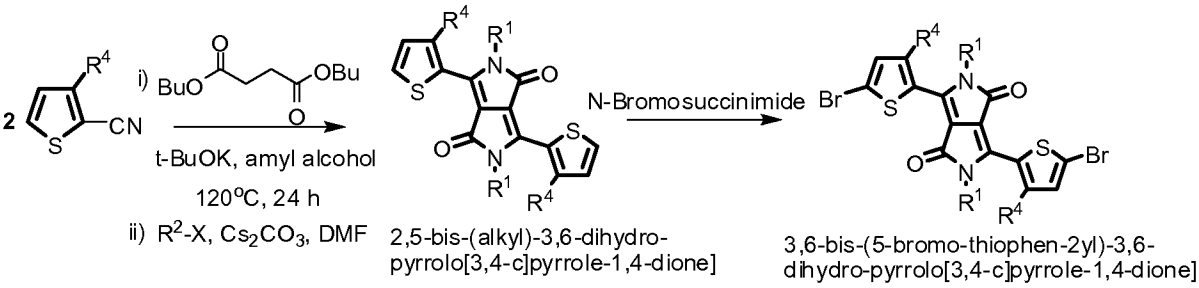
Wherein X is S, m is 1 and A is benzobisoxazole, the first compound can be synthesized according to the following scheme.



4,8-disubstitued-2,6-bis(3-substituted-5-(tribromo)thiophen-2-yl) benzo[1,2-*d*:4,5-*d'*]bis(oxazole)

4,8-disubstitued-2,6-bis(3-substituted-5-(trimethylstannyl)thiophen-2-yl) benzo[1,2-*d*:4,5-*d'*]bis(oxazole)

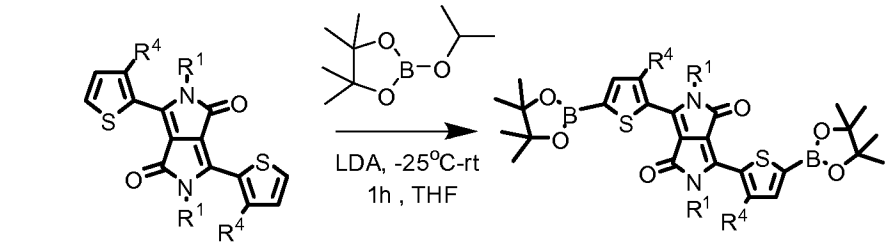
The second compound can be synthesized according to the following scheme.



2,5-bis-(alkyl)-3,6-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione]

3,6-bis-(5-bromo-thiophen-2yl)-3,6-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione]

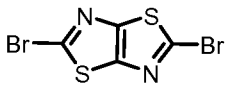
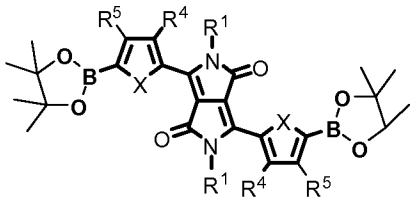
Lee *et al. Adv. Mater.* 2011, *23*, 5359-5363



N-alkyl-3,6-bis-(5-bromo-thiophen-2yl)-3,6-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione]

N-alkyl-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)thiophene-2-yl]-2,5-dihydro pyrrolo[3,4-c]pyrrole-1,4-dione

Burckstummer *et al. J. Org. Chem.* 2011, 76, 2426-2432.

Further, in some embodiments wherein m=0, the polymer described herein can be made by reacting a first compound represented by **Br—A—Br** such as  with a second compound represented by  ; wherein A, X, R^1, R^4 and R^5 have the same definitions as previously described.

ORGANIC ELECTRONIC DEVICES

The polymers described herein can be used to fabricate novel organic electronic devices, including organic light emitting diodes (OLEDs), transistors, and solar cells. The fabrication process often includes the formation of a film of the polymers described herein on a substrate, and one embodiment is a coated substrate. Organic films of the polymer described herein can be prepared by known methods such as spin coating, casting, dip coating, inkjet, doctor blade coating, screen printing, and spray coating. Using these methods, one can prepare organic films having good properties such as mechanical strength, toughness, and durability without forming cracks in the films. The organic films can be suitable for use

in organic electronic devices such as FET elements, photovoltaic cells, and light emitting elements.

Films of the copolymer described herein are typically prepared by coating a coating liquid, which is prepared by dissolving the copolymer in a solvent such as dichloromethane, tetrahydrofuran, chloroform, toluene, chlorobenzene, dichlorobenzene, or xylene, on a substrate. Specific examples of the coating methods include spray coating, spin coating, blade coating, dip coating, cast coating, roll coating, bar coating, die coating, ink jet, dispense methods, etc. In this regard, a proper method and a proper solvent can be selected taking into consideration of the properties of the polymer used. Suitable materials for use as the substrate on which a film of the polymer of the present invention is formed include inorganic substrates such as glass plates, silicon plates, ITO plates, and FTO plates, and organic substrates such as plastic plates (e.g., PET films, polyimide films, and polystyrene films) , which can be optionally subjected to a surface treatment. In many embodiments, a substrate with a smooth surface is used.

The thickness of the organic film and the organic semiconductor layer of the organic thin film transistor of the present invention are not particularly limited. However, the thickness can be determined such that the resultant film or layer is a uniform thin layer (i.e., the film or layer can be substantially free of gaps or holes which can adversely affect the carrier transport property thereof). The thickness of the organic semiconductor layer can be, for example, not greater than 1 micron, and preferably about 5-200 nm.

TRANSISTORS

Many embodiments of the devices described herein relate to a field-effect transistor comprising the copolymer described herein. In some embodiments, the field-effect transistor comprises a thin-film of the copolymer. The thin film can be deposited from a solution of the copolymer. The thin-film can be fabricated by spin coating. The thin-film can be fabricated by vacuum vapor deposition.

The field-effect transistor can be a p-channel transistor. The electron mobility of the field-effect transistor can be, for example, 1×10^{-3} cm^2/Vs or higher, or 1×10^{-2} cm^2/Vs or higher, or 0.1 cm^2/Vs or higher, or 0.3 cm^2/Vs or higher, or 0.5 cm^2/Vs or higher, or 1 cm^2/Vs or higher. The on/off current ratio of the field-effect transistor can be, for example, at least 10^4, or at least 10^5, or at least 10^6, or about 10^4-10^7, or about 10^5-10^6.

The organic thin film transistors of described herein can have a configuration such that an organic semiconductor layer including the copolymer described herein is formed

therein while also contacting the source electrode, drain electrode and insulating layer of the transistor.

The organic thin film transistor prepared above can be thermally annealed. Annealing can be performed while the film is set on a substrate, and is believed (without wishing to be bound by theory) to allow for at least partial self-ordering and/or π-stacking of the copolymers to occur in the solid state. The annealing temperature is determined depending on the property of the polymer, but is preferably from room temperature to 300 °C, and more preferably from 50 to 300 °C. In some embodiments, thermal annealing is carried out at least 150 °C, or preferably above 170 °C, or above 200 °C. When the annealing temperature is too low, the organic solvent remaining in the organic film cannot be well removed therefrom. In contrast, when the annealing temperature is too high, the organic film can be thermally decomposed. Annealing is preferably performed in a vacuum, or under nitrogen, argon or air atmosphere. In some embodiments, annealing is performed in an atmosphere including a vapor of an organic solvent capable of dissolving the polymer so that the molecular motion of the polymer is accelerated, and thereby a good organic thin film can be prepared. The annealing time can be properly determined depending on the aggregation speed of the polymer.

An insulating (dielectric) layer can be used in the organic thin film transistors comprising the copolymers described herein, situated between the gate electrode and the organic thin film comprising the polymers. Various insulating materials can be used for the insulating layer. Specific examples of the insulating materials include inorganic insulating materials such as silicon oxide, silicon nitride, aluminum oxide, aluminum nitride, titanium oxide, tantalum oxide, tin oxide, vanadium oxide, barium strontium titanate, barium zirconate titanate, lead zirconium titanate, lead lanthanum titanate, strontium titanate, barium titanate, barium magnesium fluoride, bismuth tantalate niobate, hafnium oxide, and trioxide yttrium; organic insulating materials such as polymer materials, e.g., polyimide, polyvinyl alcohol, polyvinyl phenol, polystyrene, polyester, polyethylene, polyphenylene sulfide, unsubstituted or halogen-atom substituted polyparaxylylene, polyacrylonitrile, and cyanoethylpullulan; etc. These materials can be used alone or in combination. Among these materials, materials having a high dielectric constant and a low conductivity are preferably used.

Suitable methods for forming such an insulating layer include dry processes such as CVD methods, plasma CVD methods, plasma polymerization methods, and vapor deposition methods; wet processes such as spray coating methods, spin coating methods, dip coating

methods, inkjet coating methods, cast coating methods, blade coating methods, and bar coating methods; etc.

In order to improve the adhesion between the insulating layer and organic semiconductor layer, to promote charge transport, and to reduce the gate voltage and leak current, an organic thin film (intermediate layer) can be employed between the insulating layer and organic semiconductor layer. The materials for use in the intermediate layer are not particularly limited as long as the materials do not chemically affect the properties of the organic semiconductor layer, and for example, molecular films of organic materials, and thin films of polymers can be used therefor. Specific examples of the materials for use in preparing the molecular films include coupling agents such as octadecyltrichlorosilane, octyltrichlorosilane, octyltrimethoxysilane, hexamethyldisilazane (HMDS), and octadecylphosphonic acid. Specific examples of the polymers for use in preparing the polymer films include the polymers mentioned above for use in the insulating layer. Such polymer films can serve as the insulating layer as well as the intermediate layer.

The materials of the electrodes (such as gate electrodes, source electrodes and drain electrodes) of the organic thin film transistor described herein are not particularly limited as long as the materials are electrically conductive. Specific examples of the materials include metals such as platinum, gold, silver, nickel, chromium, copper, iron, tin, antimony, lead, tantalum, indium, aluminum, zinc, tungsten, titanium, calcium, and magnesium; alloys of these metals; electrically conductive metal oxides such as indium tin oxide (ITO); inorganic or organic semiconductors, whose electroconductivity is improved by doping or the like, such as silicon single crystal, polysilicon, amorphous silicon, germanium, graphite, carbon nanotube, polyacetylene, polyparaphenylene, polythiophene, polypyrrole, polyaniline, polythienylenevinylene, polyparaphenylenevinylene, and complexes of polyethylenedioxythiophene (PEDOT) and polystyrene sulfonic acid.

SOLAR AND PHOTOVOLTAIC CELLS

Solar cells and photovoltaic cells described herein can be fabricated by first spin-coating a PEDOT buffer layer on top of ITO-coated glass substrates (10 Ω/sq, Shanghai B. Tree Tech. Consult Co. Ltd., Shanghai, China) at 3000 rpm for 40 s and drying at 150°C for 10 min under vacuum. The thickness of PEDOT can be, for example, around 40 nm.

The active layer of the solar cells comprising the polymers described herein can comprise a mixed "heterojunction" active layer that is a phase separated blend of the polymers or copolymers described herein and an electron acceptor material. The electron

acceptor material can comprise a variety of organic materials (small molecules, oligomers, polymers, or copolymers) that have a LUMO energy level that is at least about 0.2 to 0.6 eV more negative than the LUMO energy level of the copolymers described herein, and a HOMO energy level that is more negative than the HOMO energy level of the copolymers described herein. In some embodiments, the electron acceptor material can be a fullerene or a modified fullerene (e.g., C_{61}-phenyl-butyric acid methyl ester, $PC_{61}BM$, or C_{71}-phenyl-butyric acid methyl ester, $PC_{71}BM$). In some embodiments, the electron acceptor material can be an electron accepting semiconducting organic small molecule, oligomer, or polymer having appropriate LUMO and HOMO energies (at least about 0.2-0.6 eV more negative than the LUMO energy level and a more negative HOMO energy level than the HOMO energy level of the copolymers described herein). Examples of such electron acceptor materials include small molecules, oligomers, polymers, or copolymers having highly electron deficient functional groups, such as naphthalene diimide, perylene diimide, rylene, phthalimide, and related derivatives comprising electron accepting groups.

In some embodiments of the solar cells described herein, a composition comprising a solution or dispersion of one or more of the polymers or copolymers described herein and one or more acceptor materials (for example fullerene derivatives) is spin-coated on top of the PEDOT layer, for example at a speed of 1000 rpm for 30 seconds, to form a layer comprising the one or more copolymers and one or more electron accepting materials. In some embodiments, the solution or dispersion is applied using a hot solvent, and dried under vacuum immediately after the deposition the copolymers.

The coated device precursor can then be annealed, for example on a hot plate at 150±10 °C for 10 min in a glove box, to form the active layer. The active layer can also be spin-coated in air and dried in a vacuum oven without thermal annealing. The solvents used for dissolving the mixture of copolymers described herein and the electron acceptors can be chloroform, chlorobenzene, 1,2-dichlorbenzene, etc. The solvents for copolymer/fullerene blend can be a single solvent such as chloroform, chlorobenzene, 1,2-dichlorbenzene or a mixture of two or three different solvents, the second (third) solvent can be 1,8-diiodooctane, 1,8-dibromoctane, 1,8-octanedithiol, etc. Optionally, the solvents can be heated so as to increase the solubility of the polymer and/or electron acceptor, as an aid to film formation.

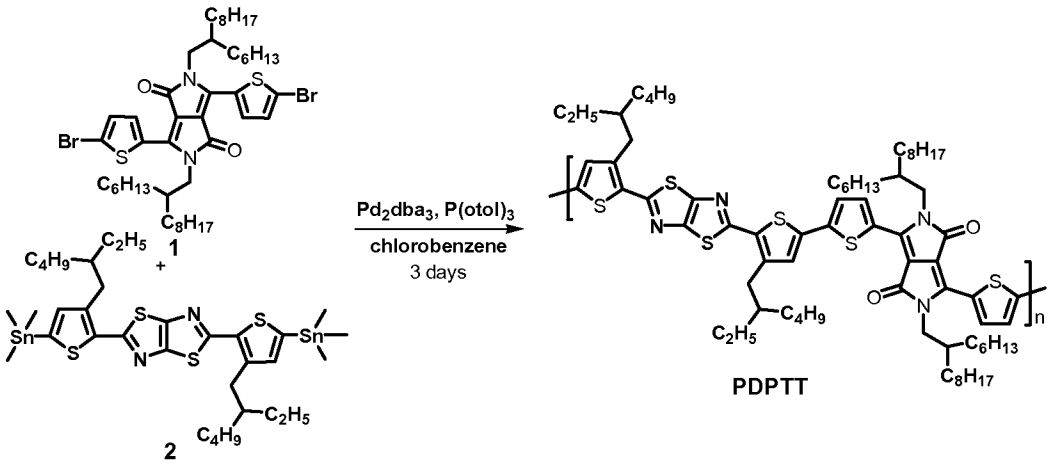
Thermal annealing is believed to induce at least partial phase separation between the polymers described herein and the electron acceptors, forming the "heterojunctions" on the nanometer scale that are believed to be the site of light-induced charge separation.

After cooling down, the solar cell precursors comprising the polymer-coated substrates can be taken out of the glove box and loaded in a thermal evaporator (BOC Edwards, 306) for the deposition of the cathode. The cathode consisting of 1.0 nm LiF and 80 nm aluminum layers can be sequentially deposited through a shadow mask on top of the active layers in a vacuum of 8×10^{-7} torr. In one embodiment, each substrate contains 4 solar cells with an active area of 9 mm^2.

Additional embodiments are provided in the following non-limiting working examples.

WORKING EXAMPLES

Example 1 - Syntheisis of PDPTT



***2,5-bis(2-hexyldecyl)-3,6-bis-(5-bromo-thiophen-2-yl)--dihydropyrrolo[3,4-c]pyrrole-1,4-dione*:** The dibromide **1** was prepared as reported in the literature (Lee *et al.*, *Adv. Mater.* **2011**, *23*, 5359-5363).

***Synthesis of 2,5-Bis-[3-(2-ethyl-hexyl)-5-trimethylstannanyl-thiophen-2yl]-thiazolo[5,4-d]thiazole*:** The distannyl compound **2** were prepared as reported in the literature (Subramaniyan *et al.*, *Adv. Ener. Mater.* **2011**, *1*, 854-860).

Syntheisis of Poly[3,6-dithiene-2-yl-2,5-di(2-hexyldecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5',5''-diyl-alt-(2,5-bis(3-ethylhexylthiophen-2yl)thiazolo[5,4-d]thiazole) (PDPTT). The starting materials **1** (398 mg, 0.4 mmol) and **2** (376 mg, 0.4 mmol), and catalyst tris(dibenzylideneacetone)dipalladium (0) (8 mg, 0.009 mmol) and tri-o-tolylphosphine (11 mg, 0.04 mmol) in anhydrous chlorobenzene (38 mL) were heated at reflux for 3 days. Then the heating was reduced to 50 °C; the reaction mixture was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 hours. The black precipitate

was collected via filtration, and was further purified by Soxhlet extraction with methanol and hexane. Then the residue was extracted with chloroform, evaporated and dried to yield a dark brown solid with a metallic appearance (400 mg, 71%). ^{1}H NMR ($CDCl_3$): 8.71-8.91 (m, 4H), 6.85-7.20 (m, 2H), 3.82-4.30 (m, 4H), 2.71-3.02 (m, 4H), 0.87-2.10 (m, 92H).

Gel permeation chromatography (GPC) studies of polymer PDPTT showed a number-average molecular weight of 18.0 kg/mol with a polydispersity of 3.3.

The thermal behavior of PDPTT copolymer was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The copolymer PDPTT showed onset thermal decomposition temperature above 396 $^{\circ}$C and no melting transition in DSC up to 300 $^{\circ}$C , suggesting that there is no substantial effect in morphology and structural order in the solid state.

PDPTT was highly soluble in almost all organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. The absorption maximum in dilute solution of $CHCl_3$ (~10^{-6}M) was found to be 686 and 736 nm (Figure 1). The absorption spectrum of the thin films was slightly red shifted and showed a peak maximum at 749 and a vibronic shoulder at 688 nm. The optical band gap measured at the absorption edge of the film was calculated to be 1.38 eV. The HOMO and LUMO energy level of PDPTT was estimated from cyclic voltammetry (CV) results (Figure 2). The onset oxidation (E_{ox}^{onset}) and reduction (E_{red}^{onset}) potential was 0.81 V and -0.80 V (versus SCE), from which the HOMO and LUMO level of the polymer were calculated to be 5.21 eV ($E_{HOMO} = eE_{ox}^{onset} + 4.4$) and 3.60 eV ($E_{LUMO} = eE_{red}^{onset} + 4.4$), respectively. The electrochemical band gap of the polymer PDPTT was 1.61 eV

To provide further insight into the morphology of the copolymer, X-ray diffraction measurement was performed on drop-cast film (from 10 mg/mL solutions in 1,2-dichlorobenzene) deposited onto a glass substrate, annealed at 180 $^{\circ}$C for 10 minutes. A weak lamellar reflection ($2\theta = 4.21^{\circ}$) with d-spacing of 21.02 A$^{\circ}$ was found which corresponds to hexyldecyl side chains of copolymer PDPTT indicating less crystallinity in polymer films.

Example 2 - Transistors and Solar Cells Comprising PDPTT

Thin film OFETs utilizing PDPTT as an organic semiconductor were fabricated in conventional top-contact, bottom-gate geometry. Gold electrodes with a thin chromium adhesive layer were patterned on top of heavily-doped silicon with silicon dioxide (t_{ox}=200 or 300 nm) substrates. The channel widths and lengths of the devices were 400 or 1000 μm and

20-100 μm, respectively. The surface of the silicon dioxide was cleaned and treated with octyltrichlorosilane (OTS8). PDPTT copolymer was spun onto hydrophobically modified oxide from a solution in 1,2,-dichlorobenzene and the resulting thin film OFETs were then annealed at 200 °C for 10 min under inert atmosphere. Devices were tested in nitrogen-filled dry box. Electrical parameters were calculated by using the standard equation for metal-oxide-semiconductor field-effect transistors in saturation region: $I_{ds}=(\mu C_o W/2L)(V_g-V_t)^2$.

The output and transfer characteristics of the OFETs are shown in Figures 3a and 3b. The PDPTT OFETs showed p-channel characteristics with a large current modulation (I_{on}/I_{off} $>10^5$). PDPTT had an average hole mobility of 0.45 cm^2/Vs . The average threshold voltage (V_t) of PDPTT was -29.3 V.

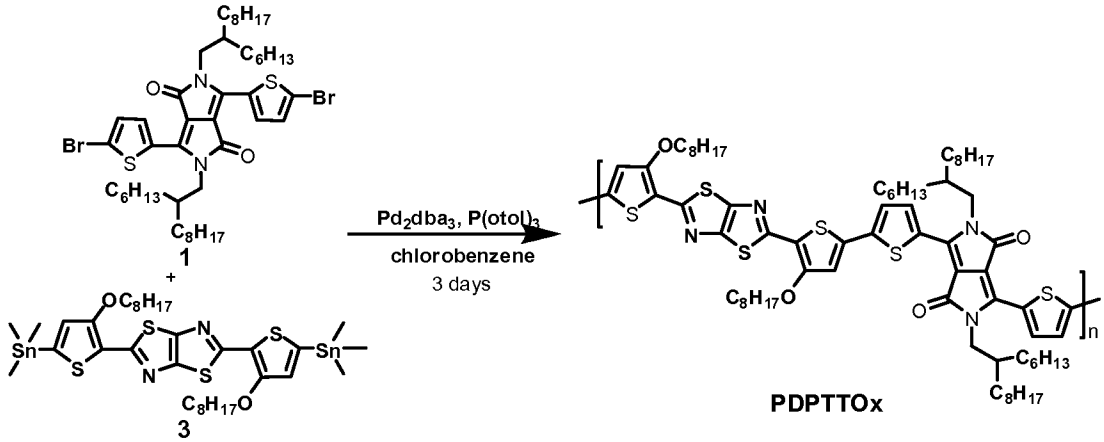
Photovoltaic cells comprising a 1:2 blend of PDPTT and $PC_{71}BM$ were fabricated. The films were spin-coated from a solution of PDPTT:$PC_{71}BM$ blend and the solvent was a mixture of *o*-dichlorobenzene (ODCB) and 1,8-diiodooctane (DIO). The blend films were dried under vacuum at room temperature for a certain period of time. UV-Vis absorption spectra PDPTT: $PC_{71}BM$ (1:2) blend films on glass/ITO/PEDOT substrates are shown in Figure 4a. Current density-voltage curves of a PDPTT:$PC_{71}BM$ (1:2) solar cell device under 100 mW/cm^2 AM1.5 solar irradiation and in the dark are shown in Figure 4b. A maximum power conversion efficiency of 3.38%, with a current density of 8.03 mA/cm^2, an open circuit voltage of 0.70 V and a fill factor of 0.60, were achieved in PDPTT:$PC_{71}BM$ solar cells.

The EQE spectra of the devices are shown in Figure 5. The PDPTT:PC $_{71}$BM device showed photoconversion efficiency with a monochromatic EQE around 30% over the 350–580 wavelength range. The calculated J_{sc} by integrating the EQE curve of PDPTT:$PC_{71}BM$ solar cell with an AM1.5G reference spectrum is 7.62 mA/cm^2 (in the wavelength range of 350–580 nm) compared with 8.0 mA/cm^2 measured on same size device; thus, the spectral mismatch factor was ~5%.

TEM image of PDPTT:$PC_{71}BM$ thin film peeled from solar cell and their SAED patterns (1:2) are shown as inset. (Figure 6). We used bright-field transmission electron microscope (BF-TEM) imaging to investigate the nanomorphology of the PDPTT:$PC_{71}BM$ blend thin films peeled off directly from the solar cells whose photovoltaic properties are discussed above. The images shown in Figure 6 were acquired at a slightly defocused condition to enhance the phase contrast between the polymer and fullerene, and under this focusing condition, fullerene domains appear darker than polymer domains due to the higher density of the fullerene. The PDPTT:$PC_{71}BM$ blend films showed a bicontinuous nanomorphology, with well-woven copolymer nanowire networks embedded in the fullerene

matrix. For example, TEM image of PDPTT:$PC_{71}BM$ blend film showed copolymer nanowires with width of 16-18 nm and length of several hundred nm, and interconnected fullerene domains with size of about 100 – 200 nm. Selected area electron diffraction (SAED) patterns shown as inset of Figure 6 indicated that the copolymer and $PC_{71}BM$ formed semi-crystalline domains, as shown by the Debye-Scherrer diffraction rings.

Example 3 - Syntheisis of PDPTTOx



Synthesis of Poly[3,6-dithiene-2-yl-2,5-di(2-hexyldecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5',5''-diyl-alt-2,5-bis(3-octyloxythiophen-2yl)-thiazolo[5,4-d]thiazole (PDPTTOx): The dibromo compound **1** (337 mg, 0.37 mmol) and distannyl compound **3** (330 mg, 0.37 mmol, prepared according to Subramaniyan *et al.*, *Adv. Ener. Mater.* **2011**, *1*, 854-860) and catalyst tris(dibenzylideneacetone)dipalladium (0) (7 mg, 0.007 mmol) and tri-o-tolylphosphine (9 mg, 0.03 mmol) in anhydrous chlorobenzene (10 mL) were heated at 120 °C for 72 hours. The temperature was then reduced to 55°C. The reaction mixture was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 hours. The brown precipitate was collected via filtration and was further purified by Soxhlet extraction with methanol, hexane and dichloromethane. The remaining solid obtained was dried under vacuum to afford PDPTTOx in 65 % yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.30-9.11 (m, 4H), 6.04-6.93 (m, 2H), 3.50-4.50 (m, 8H), 0.81-2.10 (m, 92H).

Gel permeation chromatography (GPC) studies of polymer PDPTTOx showed a number- averaged molecular weight of 17.0 kg/mol with a polydispersity of 4.0.

The thermal behavior of PDPTTOx copolymer was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Copolymer PDPTTOx showed onset thermal decomposition temperature above 378 °C and no melting transition in

DSC up to 300 °C , suggesting that there is no substantial effect in morphology and structural order in the solid state.

PDPTTOx was highly soluble in chloroform, chlorobenzene, and dichlorobenzene at room temperature. The absorption maximum in dilute solution of $CHCl_3$ (~10^{-6}M) was found to be 799 nm. The absorption spectrum of the thin films was red shifted and showed a broad absorption maximum at 769 and 818 nm. The optical band gap measured at the absorption edge of the film was calculated to be 1.22 eV. The HOMO level of PDPTTOx was estimated from cyclic voltammetry (CV) results . The onset oxidation and reduction potential was 0.74 V and -0.90 V (versus SCE), from which the HOMO and LUMO level of the polymer were calculated to be 5.14 eV and 3.50 eV, respectively. The electrochemical band gap of the polymer PDPTTOx was 1.64 eV.

To investigate the solid-state morphology and molecular organization of PDPTTOx, we performed X-ray diffraction (XRD) analysis on thin films drop-casted from a 1,2-dichlorobenzene solution onto glass substrates and annealed at 180 °C for 10 minutes. A weak lamellar reflections ($2\theta = 3.57^{o}$) with d-spacing of 24.73 A° which corresponds to hexyldecyl side chains of copolymer PDPTTOx indicating less crystallinity in thin films

Example 4 - Transistors and Solar Cells Comprising PDPTTOx

The charge transport properties of PDPTTOx were investigated by fabricating OFETs with conventional top-contact and bottom-gate geometry on top of silicon (gate) and silicon dioxide (dielectric) substrates and patterned gold source/drain electrodes. The typical output and transfer characteristics of PDPTTOx OFETs are shown in Figure 7a and 7b.

An average hole mobility (μ_h) of 1.23 cm^2/V.s was observed for transistors comprising PDPTTOx. The I_{on}/I_{off} ratios were higher than 10^5. The average threshold voltage (V_t) of PDPTTOx was -23.8 V.

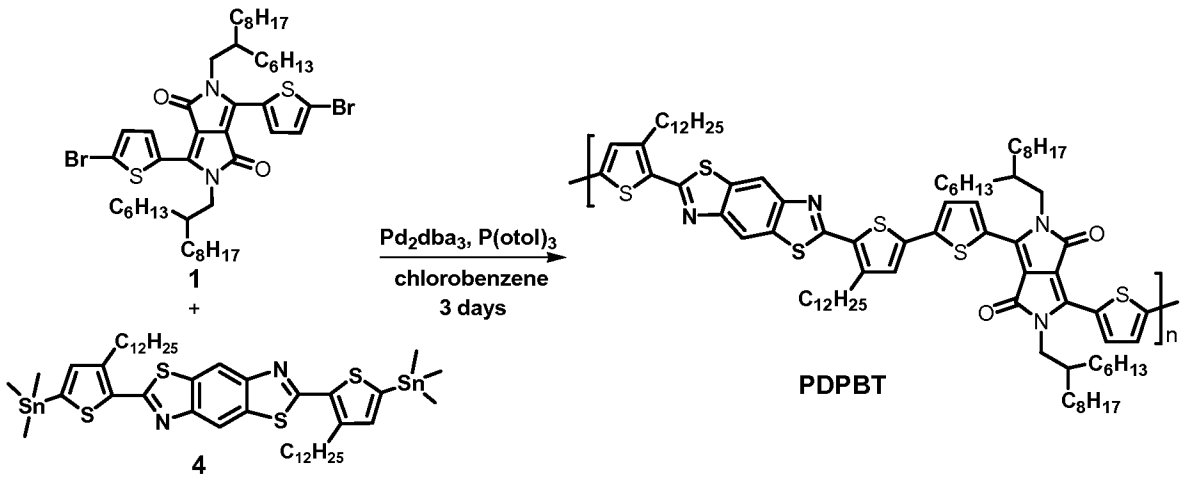
Photovoltaic cells comprising a 1:2 blend of PDPTTOx and $PC_{71}BM$ were fabricated. UV-Vis absorption spectra PDPTTOx: $PC_{71}BM$ (1:2) blend films were measured on glass/ITO/PEDOT substrates. The current density (J_{sc}), open circuit voltage (V), and fill factor (FF) achieved in the PDPTTOx:$PC_{71}BM$ (1:2) solar cell were 8.31 mA/cm^2, 0.52 V, and 0.51, respectively, with a power conversion efficiency of 2.16%.

The PDPTTOx:$PC_{71}BM$ device showed photoconversion efficiency with a monochromatic EQE around 30% over the 350–580 wavelength range. The calculated J_{sc} by integrating the EQE curve of PDPTTOx:$PC_{71}BM$ solar cell with an AM1.5G reference

spectrum is 7.68 mA/cm^2 (in the wavelength range of 350–580 nm) compared with 8.31 mA/cm^2 measured on same size device; thus, the spectral mismatch factor was ~8%.

The morphology of PDPTTOx:$PC_{71}BM$ solar cells was studied by TEM analysis (Figure 8).

Example 5 - Synthesis of PDPBT



***Synthesis of 2,6-Bis(5-trimethyltin-3-dodecylthiophen-2-yl)benzo[1,2-d;4,5-d]-Bisthiazole (4)*:** The distannyl compound **4** was prepared as reported in the literature (Ahmed *et al.*, *Macromolecules* **2011**, *44*, 7207-7219).

Synthesis of Poly[3,6-dithiene-2-yl-2,5-di(2-hexyldecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5',5''-diyl-alt-2,5-bis(3-dodecylthiophen-2yl)-benzo[1,2-d;4,5-d']bisthiazole (PDPBT): The dibromo compound **1** (380 mg, 0.42 mmol), and di-tin compound **4** (428 mg, 0.42 mmol) and catalyst tris(dibenzylideneacetone)dipalladium (0) (8 mg, 0.008 mmol) and tri-o-tolylphosphine (10 mg, 0.017 mmol) in anhydrous chlorobenzene (20 mL) were heated at reflux for 30 hours. Then the heating was reduced to 50° C; the reaction mixture was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 hours. The black precipitate was collected via filtration, and was further purified by Soxhlet extraction with methanol and hexane. Then the residue was extracted with chloroform, evaporated and dried to yield a dark brown solid (520 mg, 86%). GPC: M_n = 18.5 Kg/mol, PDI = 3.6; ^{1}H NMR ($CDCl_3$, δ ppm): 9.11- 8.72 (m, 2H), 7.61-8.51 (m, 2H), 6.90-7.50 (m, 4H), 3.90-4.10 (m, 4H), 2.60-3.10 (m, 4H), 0.82-1.91 (m, 108H).

The thermal behavior of PDPBT copolymer was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). This copolymer showed onset thermal decomposition temperature above 383 °C and no melting transition in DSC up to 300

°C, suggesting that there was no substantial effect in morphology and structural order in the solid state.

PDPBT was soluble in chloroform solution at room temperature and soluble in chlorobenzene and dichlorobenzene at 100 °C. The absorption maximum in solution in dilute $CHCl_3$ (~10^{-6}M) was found to be 668 and 723 nm. The absorption spectrum of the thin films was red shifted and showed a broad absorption maximum at 673 and 743 nm. The optical band gap measured at the absorption edge of the film was calculated to be 1.33 eV. The HOMO level of PDPBT was estimated from cyclic voltammetry (CV) results. The onset oxidation and reduction potential was 0.91 V and -0.92 V (versus SCE), from which the HOMO and LUMO level of the polymer were calculated to be 5.31 eV and 3.48 eV, respectively. The electrochemical band gap of the polymer PDPBT was 1.83 eV.

To investigate the morphology of the copolymer PDPBT, X-ray diffractions (XRD) were performed on polymer thin films. No lamellar reflections or peak was observed indicating the amorphous nature of PDPBT thin films.

Example 6 - Transistors and Solar Cells Comprising PDPBT

Transistors based on PDPBT were fabricated and tested with conventional top-contact and bottom-gate geometry on top of silicon (gate) and silicon dioxide (dielectric, t_{ox}=200–300 nm) substrates and patterned gold source/drain electrodes. The channel widths of the devices were 400–1000 μm and lengths were 20–100 μm. The surface of the silicon dioxide was cleaned and treated with octyltrichlorosilane (OTS8). Polymer solutions were spun onto a substrate. Thin films were then annealed at 200 °C for 10 min under inert atmosphere. Devices were tested in nitrogen-filled dry box. Electrical parameters were calculated by using the standard equation for metal-oxide-semiconductor field-effect transistors in saturation region: $I_{ds}=(\mu C_o W/2L)(V_g-V_t)^2$. The typical output and transfer characteristics of PDPBT OFETs are shown in Figure 24a and 24b. PDPBT showed p-channel characteristics with a large current modulation ($I_{on}/I_{off}>10^5$). The average threshold voltage (V_t) of PDPBT was -14.0 V. PDPBT had an average hole mobility of 0.0052 cm^2/Vs. Compared to the transistor comprising PDPBT, which in some embodiments serves as a comparable example, the hole mobility of transistors comprising PDPTT or PDPTTOx is substantially higher.

Solar cells using PDPBT as donor and $PC_{71}BM$ as acceptor components were fabricated. The active layer of the solar cells were spin-coated from PDPBT:$PC_{71}BM$ (1:2 wt:wt) blend solution in chloroform on top of PEDOT:PSS coated ITO substrates. The solar cell devices were finished by deposition of the cathodes, consisting of 1 nm LiF and 80 nm

Al, in a thermal evaporator. The spin-coating of the active layer was performed in a glove box and the films were annealed at 150°C for 10 min. The solar cells had an active area of 9 mm^2.

A power conversion efficiency of 2.72%, with J_{sc} of 6.79 mA/cm^2, V_{oc} of 0.79 V, and FF of 0.56, were observed in PDPBT:$PC_{71}BM$ (1:2) bulk heterojunction solar cells.

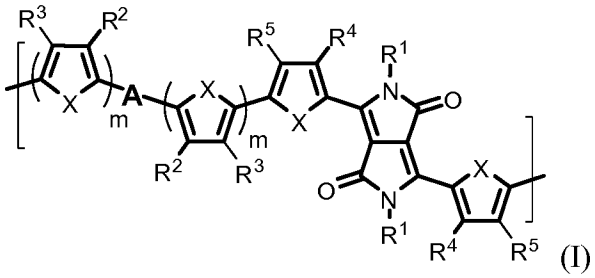
The PDPBT:$PC_{71}BM$ device showed photoconversion efficiency with a monochromatic EQE around 30% over the 350–600 wavelength range. The calculated J_{sc} by integrating the EQE curve of PDPBT:$PC_{71}BM$ solar cell with an AM1.5G reference spectrum was 6.43 mA/cm^2 (in the wavelength range of 350–580 nm) compared with 6.79 mA/cm^2 measured on same size device; thus, the spectral mismatch factor was ~6%.

MATERIALS AND METHODS

All commercially available reagents were purchased from Sigma-Aldrich, Across, Alfa-Aesar and TCI America Laboratory of chemicals. FT-IR spectra were obtained from Perkin Elmer 1720 FT-IR spectrophotometer with KBr pellets. Mass spectra were recorded on a Bruker Esquire LC/ Ion Trap Mass spectrometer. ^{1}H-NMR spectra were recorded on a Bruker AV300/AV500 at 300 MHz/500 MHz respectively using $CDCl_3$ or $C_6D_4Cl_2$ or CF_3COOD as the solvents. Gel Permeation Chromatography (GPC) analysis was performed using Polymer Lab Model 120 Gel Permeation Chromatograph (DRI / High Sensitivity Refractive Index Detector and PL-BV400HT Viscometer) against polystyrene standards in chlorobenzene at 60 °C. Thermogravimetric analysis (TGA) analysis was conducted with a TA Instruments Q50 TGA at a heating rate of 10 °C/min under a nitrogen gas flow. Cyclic voltammetry was done on an EG&G Princeton Applied Research Potentiostat/Galvanostat 273A. A three-electrode cell was used, using platinum wire electrodes as both counter and working electrode. Silver/silver ion (Ag in 0.1 M $AgNO_3$ solution, Bioanalytical System, Inc.) was used as a reference electrode. Ferrocene/ferrocenium (Fc/Fc^+) was used as an internal standard. The potential values obtained in reference to Ag/Ag^+ were converted to the saturated calomel electrode (SCE) scale. Thin film cyclic voltammetry was performed in acetonitrile containing 0.1M $TBAPF_6$. UV-vis absorption spectra were recorded on a Perkin-Elmer model Lambda 900 UV/vis/near-IR spectrophotometer. The photoluminescence (PL) emission spectra were obtained with a Photon Technology International (PTI) Inc. model QM2001-4 spectrofluorimeter. Thin film of polymer was drop-cast on a freshly cleaned glass substrate for X-ray diffraction (XRD). XRD patterns were obtained on a Bruker AXS D8 Focus diffractometer with Cu Kα beam (40 kV, 40 mA; $\lambda = 0.15418$ nm).

WHAT IS CLAIMED IS:

1. A polymer comprising a first repeating unit of formula (I)



(I)

wherein:

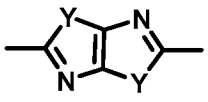
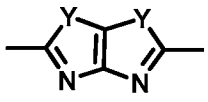
(i) X at each occurrence is independently selected from O, S and Se;

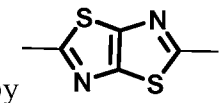
(ii) m is 0, 1, 2 or 3;

(iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group;

(iv) the polymer has a M_w of 40,000 Da or more; and

(v) A is an electron withdrawing group represented by

 or  , wherein (a) Y at each occurrence is independently selected from O, S, Se and N(R^6); and (b) R^6 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} linear, branched or cyclic organic group.

2. The polymer of claim 1, wherein A is represented by 

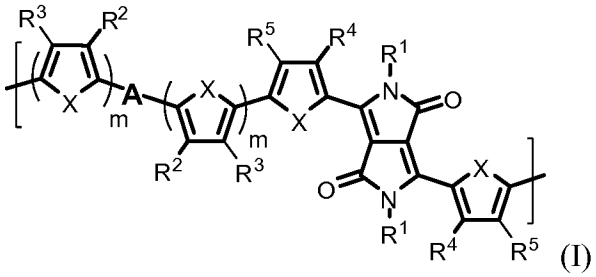
3. The polymer of claim 1 or 2, wherein X is S.

4. The polymer of any of claims 1-3, wherein m is 1.

5. The polymer of any of claims 1-4, wherein R^1 at each occurrence is independently selected from hydrogen, optionally substituted alkyl, optionally substituted heteroalkyl, fluoroalkyl, fluoroheteroalkyl; and wherein R^2, R^3, R^4 and R^5 at each occurrence is independently selected from hydrogen, halogen, cyano, optionally substituted alkyl, fluoroalkyl, optionally substituted alkoxy, fluoroalkoxy, optionally substituted thioalkyl, fluorothioalkyl, optionally substituted alkyl sulfoxide, fluoroalkyl sulfoxide, optionally substituted alkyl sulfone, and fluoroalkyl sulfone.

6. The polymer of any of claims 1-5, wherein R^1 at each occurrence is independently selected from C_4-C_{30} linear, branched or cyclic alkyl, wherein R^2 at each occurrence is independently C_4-C_{30} linear or branched alkoxy, and wherein R^3, R^4 and R^5 at each occurrence is H.

7. A polymer comprising a first repeating unit of formula (I)



(I)

wherein:

(i) X at each occurrence is independently selected from O, S and Se;

(ii) m is 0, 1, 2 or 3;

(iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence are independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group;

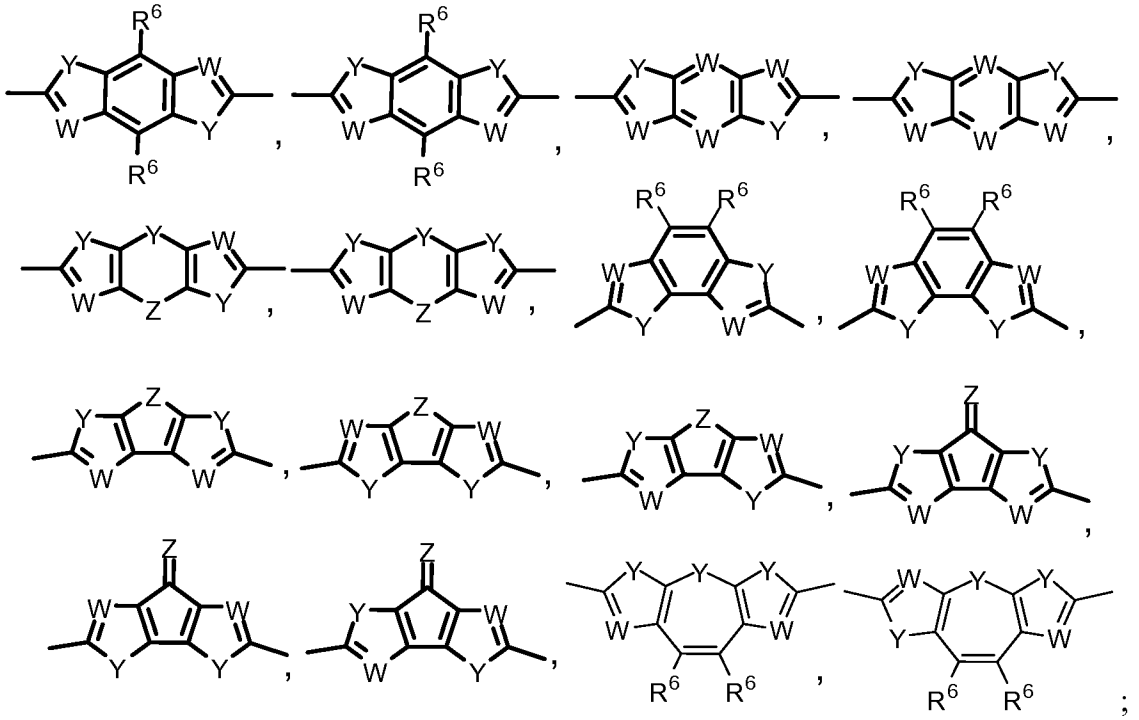
(iv) the polymer has a M_w of 40,000 Da or more; and

(v) A is an electron withdrawing group comprising two or more rings fused together, with two of said rings each comprising at least one imine group.

8. The polymer of claim 7, wherein A comprises at least two thiazole rings.

9. The polymer of claim 7 or 8, wherein A comprises three or more rings fused together.

10. The polymer of any of claims 7-9, wherein A is selected from



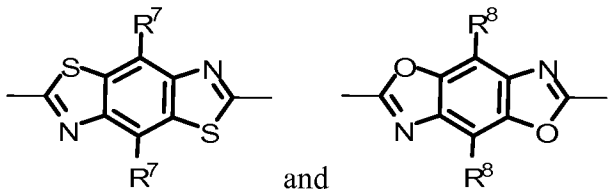
wherein:

(i) W at each occurrence is independently selected from N and C(R^6);

(ii) Y and Z at each occurrence is independently selected from O, S, Se, P(R^6), P(O)R^6, Si(R^6)$_2$, C(R^6)$_2$ and N(R^6); and

(iii) R^6 at each occurrence is independently selected from hydrogen, halogen, hydroxyl, cyano, nitro, silyl, siloxanyl, and optionally substituted C_1-C_{30} linear, branched or cyclic organic group.

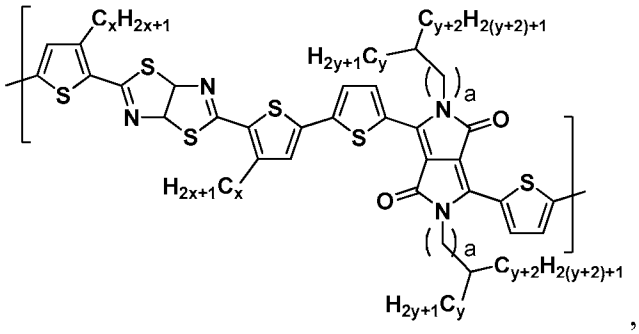
11. The polymer of any of claims 7-10, wherein A is selected from

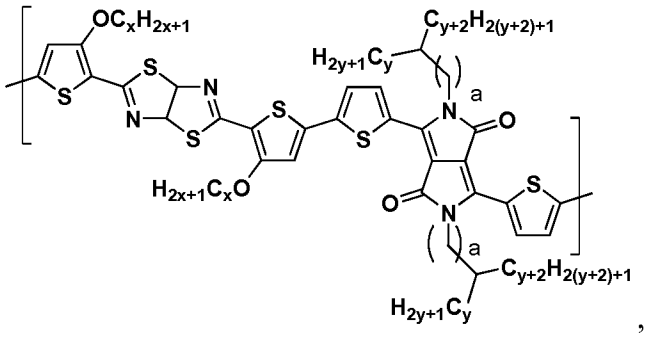


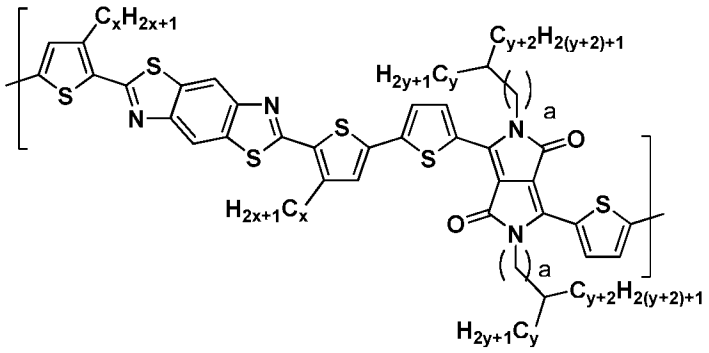
and

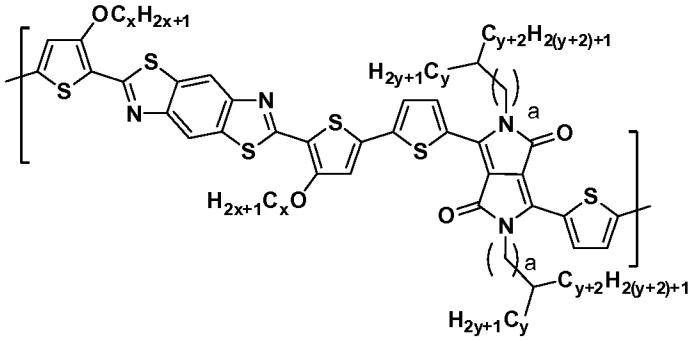
, wherein R^7 and R^8 at each occurrence is independently selected from hydrogen, halogen, cyano, and optionally substituted C_4-C_{30} organic group.

12. The polymer of any of claims 1-11, wherein the first repeating unit is selected from


,

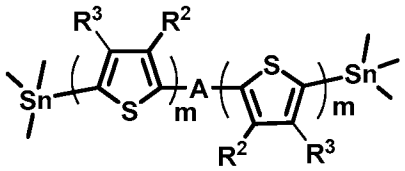
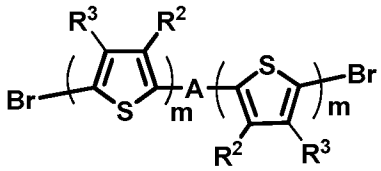

,


, and

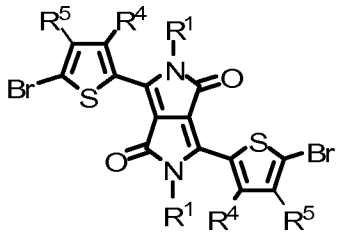
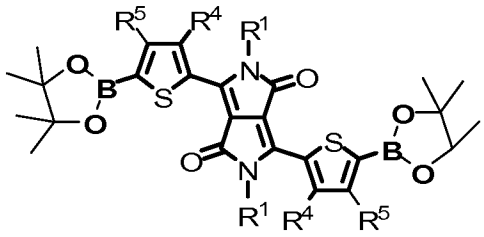

; wherein x and y are 2-16, a is 1-15.

13. The polymer of any of claims 1-12, wherein the polymer consists essentially of the first repeating unit.

14. A method for making the polymer of any of claims 1-13, comprising copolymerizing a first compound represented by

or with a second compound

represented by or ;

wherein:

(i) X at each occurrence is independently selected from O, S and Se;

(ii) m is 0, 1, 2 or 3;

(iii) R^1 at each occurrence is independently selected from hydrogen and optionally substituted C_1-C_{30} organic group; R^2, R^3, R^4 and R^5 at each occurrence are independently selected from hydrogen, halogen, cyano, and optionally substituted C_1-C_{30} organic group; and

(iv) A is an electron withdrawing group comprising two or more rings fused together, with two of said rings each comprising at least one imine group.

15. A composition comprising the polymer of any of claims 1-13 or made by the method of claim 14.

16. An electronic device comprising the polymer of any of claims 1-13 or made by the method of claim 14, or the composition of claim 15.

17. A p-channel transistor comprising a semiconducting layer, wherein said layer is obtained by solution processing and annealing a composition, and wherein said composition comprises at least one solvent and the polymer of any of claims 1-13 or made by the method of claim 14, and wherein the transistor has a field effect carrier mobility of 0.3 cm^2/Vs or more.

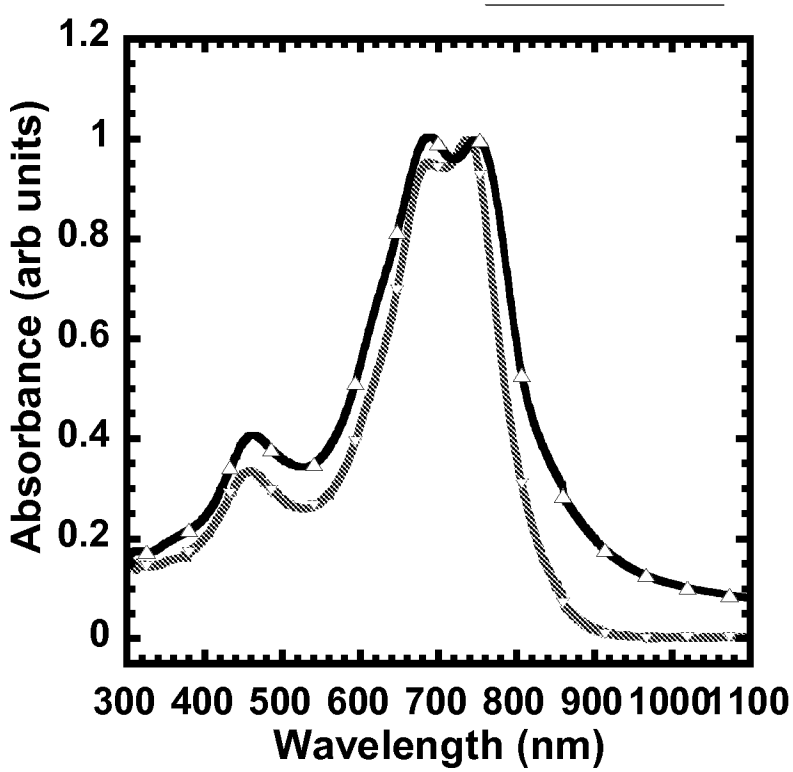

Absorbance (arb units)
1.2
1
0.8
0.6
0.4
0.2
0
300 400 500 600 700 800 900 1000 1100
Wavelength (nm)

Figure 1

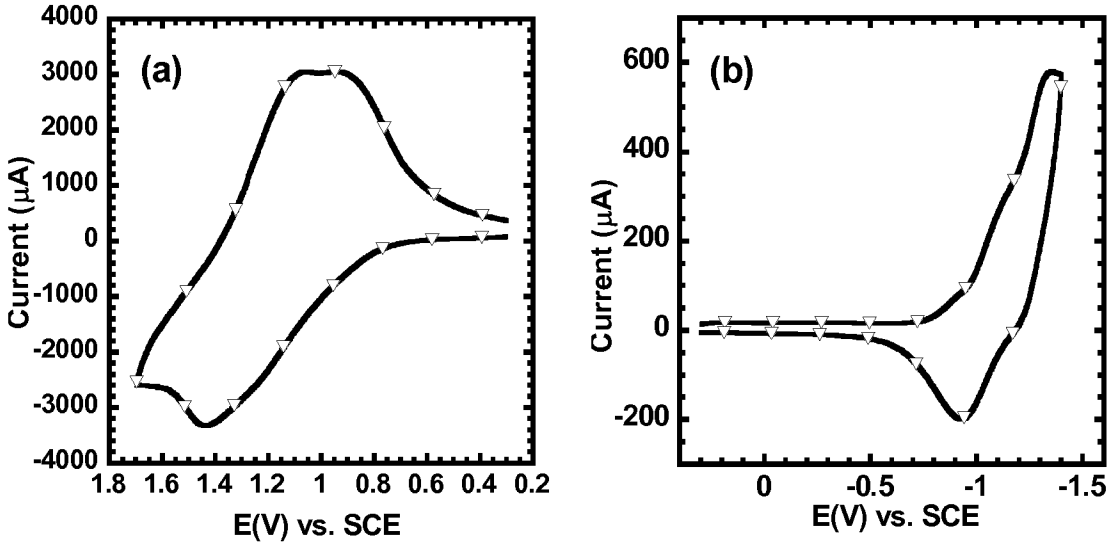

(a)
Current (μA)
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
1.8 1.6 1.4 1.2 1 0.8 0.6 0.4 0.2
E(V) vs. SCE
(b)
Current (μA)
600
400
200
0
-200
0 -0.5 -1 -1.5
E(V) vs. SCE

Figure 2

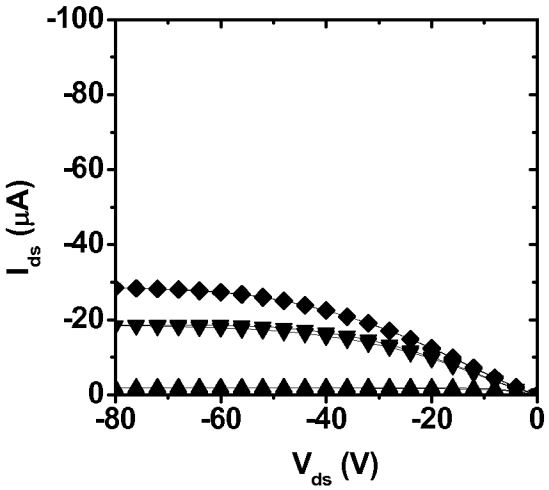


Figure 3a

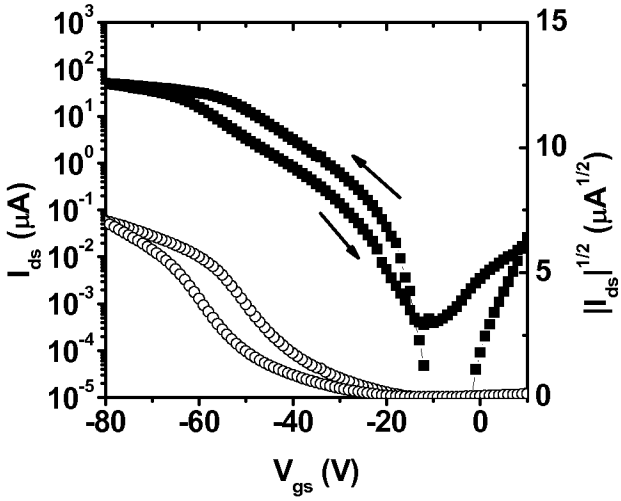


Figure 3b

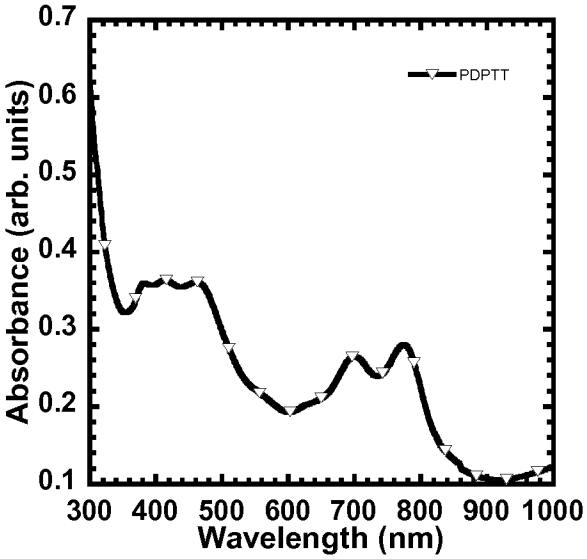


Figure 4a

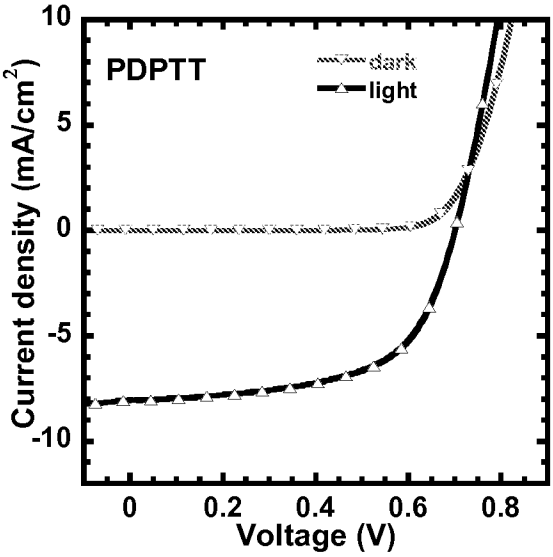


Figure 4b

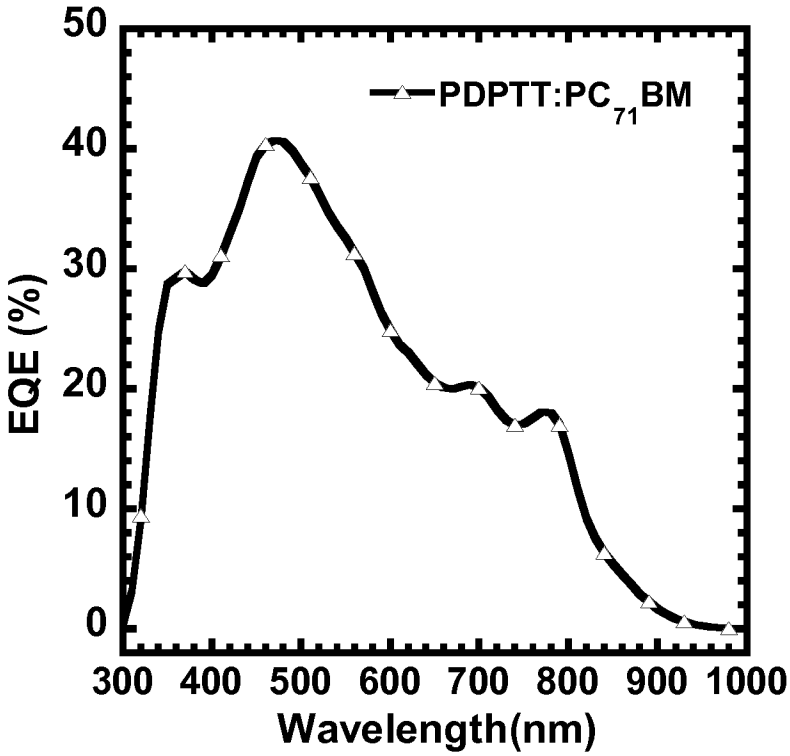

PDPTT:PC71BM
EQE (%)
Wavelength(nm)
0
10
20
30
40
50
300
400
500
600
700
800
900
1000

Figure 5

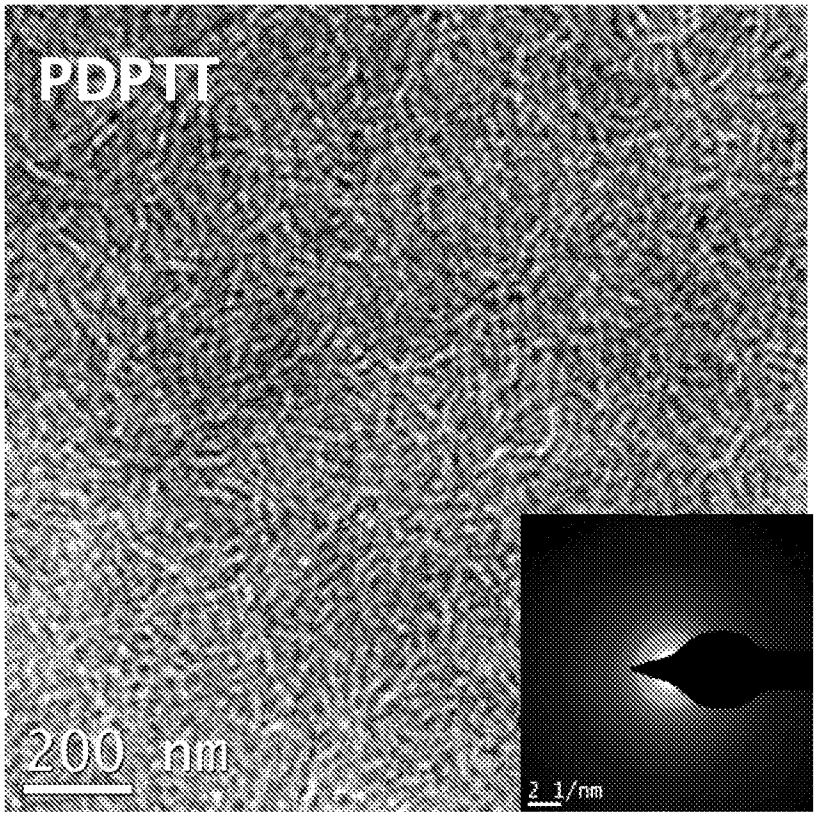


Figure 6

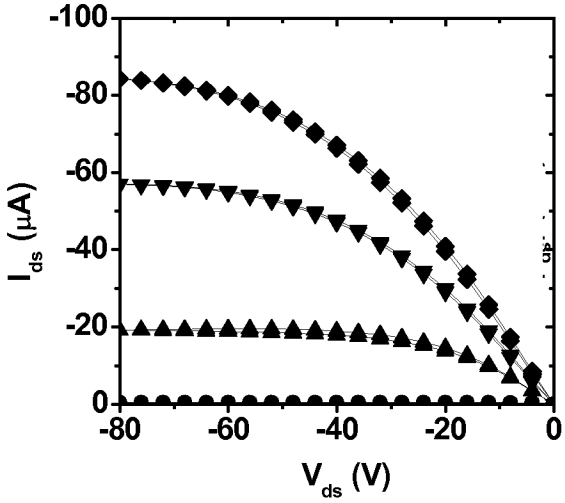


Figure 7a

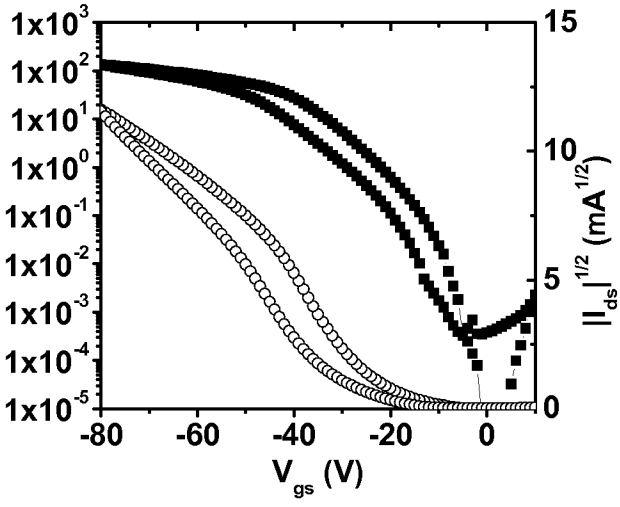


Figure 7b

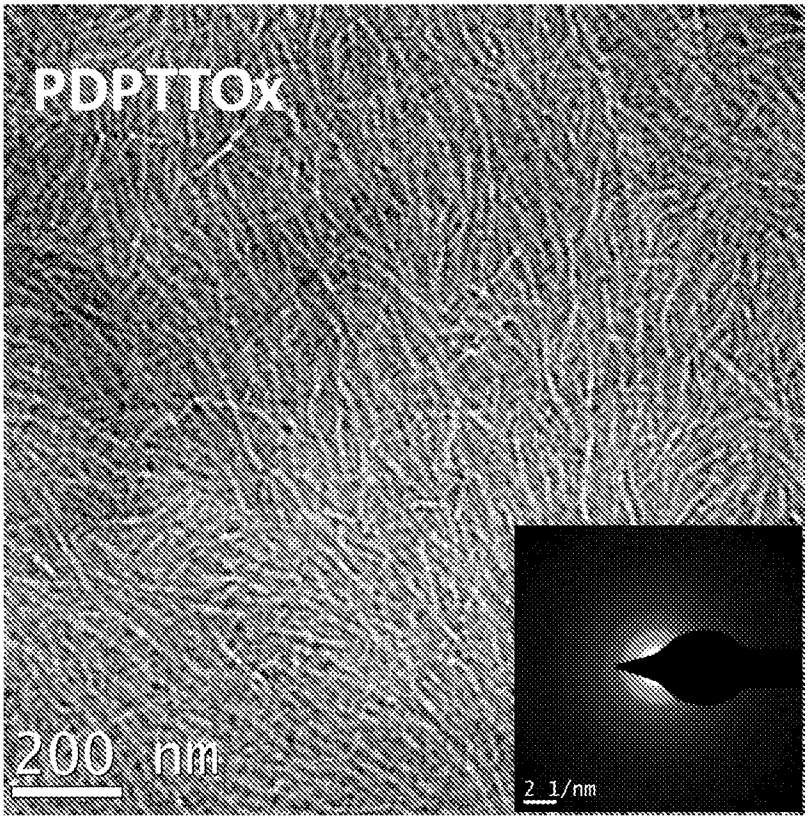


Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055967

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/302311 A1 (TURBIEZ MATHIEU G R [FR] ET AL) 10 December 2009 (2009-12-10) paragraphs [0087], [0121]	1-17
X	US 2011/215313 A1 (DUEGGELI MATHIAS [CH] ET AL) 8 September 2011 (2011-09-08) paragraph [0080]	1-8, 12-17

-/--

[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
6 December 2013	20/12/2013

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055967

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	SELVAM SUBRAMANIYAN ET AL: "High Mobility Thiazole-Diketopyrrolopyrrole Copolymer Semiconductors for High Performance Field-Effect Transistors and Photovoltaic Devices", MACROMOLECULES, vol. 45, no. 22, 5 November 2012 (2012-11-05), pages 9029-9037, XP055082910, ISSN: 0024-9297, DOI: 10.1021/ma301660j the whole document	1-17
X	US 2012/186652 A1 (PAN HUALONG [US] ET AL) 26 July 2012 (2012-07-26) examples 2A-2K; compounds VIa-VIIIa	1-17
X	JAE WOONG JUNG ET AL: "A high mobility conjugated polymer based on dithienothiophene and diketopyrrolopyrrole for organic photovoltaics", ENERGY & ENVIRONMENTAL SCIENCE, vol. 5, no. 5, 1 January 2012 (2012-01-01) , page 6857, XP055082921, ISSN: 1754-5692, DOI: 10.1039/c2ee21149a the whole document	1-17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/055967

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-6, 12(completely); 7, 8, 13-17(partially)

   A diketopyrrolopyrrole-based polymer comprising an electron withdrawing group consisting of an annealed heteroaromatic ring system consisting of two rings.

   ---

2. claims: 9-11(completely); 7, 8, 12-17(partially)

   A diketopyrrolopyrrole-based polymer comprising an electron withdrawing group consisting of an annealed heterocyclic system consisting of three rings.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/055967

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009302311 A1	10-12-2009	AU 2007263828 A1	03-01-2008
		BR PI0713952 A2	04-12-2012
		CA 2655076 A1	03-01-2008
		EP 2035428 A1	18-03-2009
		JP 2009541548 A	26-11-2009
		KR 20090024832 A	09-03-2009
		TW 200811214 A	01-03-2008
		US 2009302311 A1	10-12-2009
		WO 2008000664 A1	03-01-2008
US 2011215313 A1	08-09-2011	CN 102203160 A	28-09-2011
		EP 2350160 A1	03-08-2011
		JP 2012506930 A	22-03-2012
		KR 20110093820 A	18-08-2011
		TW 201026738 A	16-07-2010
		US 2011215313 A1	08-09-2011
		WO 2010049323 A1	06-05-2010
US 2012186652 A1	26-07-2012	NONE	