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(54) Title: CONJUGATED COPOLYMERS USEFUL IN ELECTRONICS

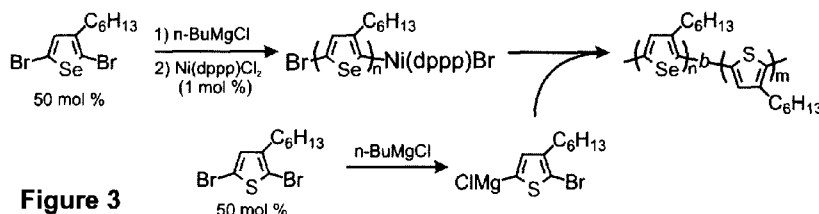


Figure 3

(57) Abstract: Selenophene-thiophene copolymers as a class of conjugated copolymers that exhibit broad light absorption properties. Phase-separated domains of block copolymers are observed in the solid-state. Scanning transmission electron microscopy and topographic elemental mapping shows that domains are either rich in selenophene or thiophene, indicating that blocks of distinct heterocycles preferentially associate with one another in the solid-state. By mixing these block copolymers with NCs, a surprising co-self-assembly of NCs and polymer is observed. Scanning transmission electron microscopy (STEM) and elemental linescan experiments show that the NCs selectively associate with the S-rich phase to arrange into networks of linear structures. Photoluminescence (PL) quenching experiments show efficient excitation energy transfer between NCs and polymer nanofibers. Manufacture and use of semiconductor composite materials using the copolymers is described.

CONJUGATED COPOLYMERS USEFUL IN ELECTRONICS

This application claims the benefit of priority of U.S. Provisional patent application No. 61/492,588 filed June 2, 2011, and U.S. Provisional patent application No. 61/553,638 filed October 30, 2011, the specifications of which are
5 incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

Copolymers having a conjugated backbone are disclosed. The copolymers are useful as e.g., semiconductors. A specific copolymer is a selenophene-thiophene block copolymer, which can be incorporated as part of a composite material in
10 combination with an electron acceptor such as a fullerene, quantum dot, etc. Composite materials can be used as the active semiconducting material in a solar cell.

BACKGROUND

Fully conjugated polymers are useful because they are generally electrically
15 conductive, and can be used in the making of a variety of electronic devices. Approaches to controlling the optical and morphological properties of conjugated polymer include controlling polymer regioregularity, annealing, patterning, or processing with additives.² Controlling phase separation is perhaps the most attractive approach because it is a spontaneous process that offers significant
20 control over nanoscale structure and can be effected in a rational chemical manner. From a device standpoint, nanoscale phase separation achieves morphologies that facilitate charge transfer and charge transport.^{1,2} In general, polymers can be designed to phase separate by synthesizing copolymers that contain blocks with distinct functional groups.³ While this strategy has been demonstrated in a variety of
25 nonconjugated polymers (which are generally nonconductive, as opposed to fully conjugated polymers, which generally are), there are far fewer ways to design and synthesize distinct block structures and hence control phase separation in conjugated polymers.

Conjugated/nonconjugated block copolymers can be prepared, however, they
30 require the incorporation of insulating segments into the polymer system.⁴ Fully

conjugated block polythiophenes have been synthesized where each block contains a unique alkyl side chain.⁵ Side chains mainly control intermolecular interactions, which influence properties; however, this is primarily an indirect and unpredictable way to control optical properties.

5 It would be very advantageous to provide a method for controlling optical properties and nanostructure of fully conjugated polymers such that the polymers and composites made therefrom have applicability to a wide range of electronics applications.

SUMMARY

10 Herein are disclosed phase separable block copolymers comprising at least two distinct fully conjugated homopolymers, wherein each distinct homopolymer comprises a distinct repeated monomer, and wherein each distinct monomer of each distinct homopolymer comprises a distinct heterocycle. Because of the use of the distinct heterocycles, these copolymers are fully conjugated (and therefore favorable
15 for use in electronic devices). The presence of the distinct heterocycles also leads to a surprising self-assembly of the copolymer into distinct domains upon phase separation. This self-assembly is surprising because thiophene and selenophene are quite similar in structure. Therefore, the optical and morphological properties of these block copolymers can be controlled.

20 Unique chemical compounds termed selenophene-thiophene block copolymers were synthesized as the first proof-of-principle of this new class of block copolymers. By mixing these block copolymers with nanocrystals (NCs), a surprising co-self-assembly of NCs and polymer was observed. Photoluminescence (PL) quenching studies show efficient excitation energy transfer between NCs and
25 polymer nanofibers. Both the block copolymer and the nanocrystal-copolymer composite have useful applications applicable to a wide range of electronics applications.

Organic solar cell (OSC) technology is considered a next-generation solar energy technology due to the potential for lightweight, low-cost and flexible devices.
30 Central to the development of the technology are efforts to produce new compositions that can (1) be synthesized and processed more cheaply; and (2) improve the performance characteristics of solar devices. Because of the anticipated

commercial value as well as the interesting physical processes that govern the operation of such devices, OSCs have received increasing attention and have been developed rapidly during the past two decades¹⁻⁶. For example, Schilinsky et al. and coworkers disclosed a device with 2.8% power conversion efficiency (PCE) in 2002 which was composed of a thiophene polymer⁷. Since then, device efficiency of this composition has been improved to 5%⁸. Currently, typical solar efficiencies for organic photovoltaics (OPV) lie in the range of 1-5%⁹⁻¹¹. Viable commercial devices have been achieved at ~2% module efficiency according to recent reports¹²⁻¹⁶. To further boost device performance, more efficient polymer material is a key factor. Such efforts include selenophene polymer, which was disclosed by Ballantyne et al. in 2007 with device efficiency of 2.7%¹⁷.

In addition to copolymers of the invention disclosed herein, a method for making a photovoltaic device is disclosed. The method includes (i) providing a solution of a block copolymer of the invention; and (ii) applying the solution to a substrate. One or the other or both of the solution and substrate is controlled to be at least 40°C, as for example by heating, during the step of applying the solution to the substrate.

The temperature of the solution and/or substrate is preferably between 50°C and 100°C, or 50° and 90°C, or 60°C and 90°C, or 70°C and 90°C. A suitable temperature in a particular embodiment described below was found to be around 80°C, and both the substrate and solution were heated to be about this temperature when applying the solution to the substrate. In a particular embodiment, both the copolymer solution and the substrate are heated during the application step.

According to such method, the copolymer is usually applied to form a film on the substrate to which it directly adheres. Preferably, conditions are controlled such that the film is made up of fibers of the block copolymer, the fibers having a thickness of from 5 to 500 nm, more preferably between 5 and 50 nm, and they can be between 5 and 40 nm or between 5 and 30 nm or 5 and 20 nm or between 10 and 20 nm. Fibers spacing of 10 to 20 nm was obtained.

The temperature of the solution and/or the substrate can be controlled during the application process to form a film having an average roughness (Ra) of less than 8, 7, 6, 5 4 or 3 nm, and is typically greater than 0.1 or 0.3 or 0.5 nm. It is thought an

Ra close to about 1 nm e.g., about 0.7 nm can provide an OSC having a suitable power conversion efficiency. Ra can be in the range of 0.1 to 8, or 0.3 to 7, or 0.3 to 6 or 0.5 to 6, or 0.5 to 5, or 0.5 to 4 or 0.5 to 3 or 0.7 to 4 nm.

In certain embodiments, the film is dried shortly or immediately after application of the copolymer solution. The temperature can be equal to or greater than the temperature of the solution that was applied, and/or the temperature of the substrate during the application step.

In certain embodiments, the film is maintained at a temperature greater than or equal to the temperature of step (i) throughout step (ii) and the step of drying the film.

It is also possible to obtain a film using a process of this invention in which the film has a nanomorphology that is thermally stable between 25°C and 350°C, 25 and 250°C, 25 and 200°C, 25 and 150°.

An electrode can be installed in contact with the film in the manufacture of a solar cell.

A substrate typically comprises a conductor layer such as indium tin oxide coated with PEDOT:PSS. Preferably, a copolymer solution is applied directly to the conductor layer.

In preferred solar cell embodiments, the polymer solution includes admixed therewith an electron acceptor. An electron acceptor can be one or more of a fullerene, a fullerene derivative, a nanoparticle, nanocrystal, quantum dot, etc. Exemplary quantum dots include one or more of e.g., CdSe, CdTe, CdS, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, Cd₃P₂.

A preferred photovoltaic device is a solar cell having a power conversion efficiency of at least 2.7% when exposed to simulated sunlight of an intensity of 1 Sun under AM1.5 G conditions. In a preferred embodiment, the film is formed in accordance with a method described above, and thus includes a copolymer film having a suitable Ra obtainable by the method. The film can comprise fibers of copolymer having a suitable or optimized average thickness obtainable by the method. As a solar cell, the film would also include an electron acceptor incorporated into and throughout the film formed on the substrate.

The entire disclosures of all applications, patents and publications cited herein are hereby incorporated by reference. This invention may also be said broadly to be composed of the parts, elements and features referred to or indicated herein, individually or collectively, in their various possible combinations.

5 A further understanding of the functional and advantageous aspects of certain embodiments of the invention can be realized by reference to the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments will now be described, by way of example only, reference being
10 made to the accompanying drawings, in which:

Figure 1 is a scheme showing the polymer structure and depicting the self-assembly of selenophene-thiophene block copolymers with and without CdSe NCs.

Figure 2 is a scheme depicting the synthesis of selenophene monomers.

Figure 3 is a scheme depicting the synthesis of the block copolymer.

15 **Figure 4** shows the ^1H NMR spectra of the statistical polymer, P3HT (poly-3-hexylthiophene), P3HS (poly-3-hexylselenophene), selenophene:thiophene copolymer, and selenophene:thiophene short-chain polymer ("oligomer"), from top to bottom in the figure.

Figure 5 shows a) absorbance, b) emission spectra of block and statistical
20 copolymers in solution, as well as absorbance of c) block and d) statistical copolymers as thin films after annealing. Corresponding homopolymers are included for reference.

Figure 6 shows atomic force microscopy (AFM) height and phase (inset)
images of a) block b) statistical copolymers and c) blended homopolymers.

25 **Figure 7** shows scanning transmission electron microscopy (STEM) elemental mapping image of block copolymer.

Figure 8 shows the ^1H NMR spectra of the 77:23 selenophene-thiophene block copolymer.

Figure 9 shows a) dark-field STEM images of polymer nanofibers self-
30 assembled with (a-e) and without (f, g) CdSe NCs.

Figure 10 shows dark-field STEM image and elemental linescan of a poly(selenophene)-*b*-poly(thiophene) film showing selenium, sulfur, and titanium

content as a function of position.

Figure 11 shows dark-field STEM image and elemental linescan of a poly(selenophene)-*b*-poly(thiophene)/CdSe film showing selenium, cadmium, and titanium content as a function of position.

Figure 12 shows (a) the wide-angle X-ray scattering (WAXS) spectra of selenophene-thiophene block copolymers with (lower curve) and without (upper curve) CdSe NCs; and (b) photoluminescence spectra of selenophene-thiophene block copolymer (1.2% (w/w)) with CdSe NCs (lower curve) and CdSe NCs (upper curve), taken at 475nm excitation.

Figure 13 shows the absorbance spectra (a) of a neat CdSe film (black) and a 1.2% (w/w) CdSe/poly(selenophene)-*b*-poly(thiophene) blend (grey). The dashed lines show the excitation lines that were used in photoluminescence experiments. Photoluminescence spectra with excitation at 400 nm (b), 440 nm (c), and 530 nm (d) of neat CdSe films (black) and 1.2% (w/w) CdSe/ poly(selenophene)-*b*-poly(thiophene) blends (grey).

Figure 14 shows the photoluminescence (PL) spectra of (from top to bottom in the figure) neat CdSe NCs, and polyselenophene-, poly(selenophene)-*b*-poly(thiophene)- and polythiophene-NC blends.

Figure 15 is a schematic of a typical OSC device incorporating a composite material of the invention.

Figure 16 shows typical I-V characteristics of P3HS-*b*-P3HT:PCBM devices prepared at different annealing times and temperatures.

Figure 17 is a typical EQE spectrum of a P3HS-*b*-P3HT:PCBM device annealed at 100°C for 10 minutes.

Figure 18 shows power conversion efficiencies of P3HS-*b*-P3HT:PCBM devices annealed at 100°C as a function of annealing time.

Figure 19 shows AFM height (a, b, c) and phase (d, e, f) images of P3HS-*b*-P3HT:PCBM films without annealing (a, d), annealed at 80 °C (b, e), and annealed at 130 °C (c,f) for 30 min.

Figure 20 shows normalized PCE as a function of post-annealing temperature of P3HS-*b*-P3HT:PCBM (squares) and P3HT:PCBM (triangles) devices. The annealing time at each temperature is 10 minutes.

Figure 21 shows PCE as a function of post-annealing time of P3HS-*b*-P3HT:PCBM (squares), P3HS:P3HT:PCBM (circles), and P3HT:PCBM (triangles) devices. The annealing temperature is 80 °C.

Figure 22 shows I-V characteristics of P3HS-*b*-P3HT:PCBM (upper plot) and P3HT:PCBM (lower plot) devices after post-annealing at 80°C for 0, 5, 10, 20 and 30 minutes, the plots for the listed times appearing in the direction of the arrow.

Figure 23 shows typical I-V characteristics of P3HS-*b*-P3HT:CdSe devices prepared under different conditions.

Figure 24 is a typical EQE spectrum of a P3HS-*b*-P3HT:CdSe devices.

DETAILED DESCRIPTION

Various embodiments and aspects of the disclosure will be described with reference to details discussed below. The following description and drawings are illustrative of the disclosure and are not to be construed as limiting the disclosure. Numerous specific details are described to provide a thorough understanding of various embodiments of the present disclosure. However, in certain instances, well-known or conventional details are not described in order to provide a concise discussion of embodiments of the present disclosure.

As used herein, the terms, “comprises” and “comprising” are to be construed as being inclusive and open ended, and not exclusive. Specifically, when used in this specification including claims, the terms, “comprises” and “comprising” and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

As used herein, the term “exemplary” means “serving as an example, instance, or illustration,” and should not be construed as preferred or advantageous over other configurations disclosed herein.

As used herein, the terms “about” and “approximately”, when used in conjunction with ranges of dimensions of particles, compositions of mixtures or other physical properties or characteristics, are meant to cover slight variations that may exist in the upper and lower limits of the ranges of dimensions so as to not exclude embodiments where on average most of the dimensions are satisfied but where statistically dimensions may exist outside this region. It is not the intention to exclude

embodiments such as these from the present disclosure.

As used herein, the phrase "homopolymer" means a polymer comprising only a single type of repeated monomers.

As used herein, the phrase "block copolymer" means a polymer formed by covalently bonding together of two or more distinct homopolymers ("blocks"). A diblock copolymer is one that is formed by two distinct homopolymers. A triblock copolymer is formed by three distinct homopolymers. Block copolymers containing more than three distinct homopolymers are also possible.

"Alkyl" includes hydrocarbon structures having 1 to 100 carbon atoms, more preferably, 1 to 50, or 1 to 30 carbon atoms, preferably 1 to 25 carbon atoms, but may contain 1 to 20, 1 to 15, 1 to 10, more preferably 1 to 8 carbon atoms or 1 to 6 carbon atoms. An alkyl group or radical may be "linear alkyl" or "branched alkyl". For any use of the term "alkyl", unless clearly indicated otherwise, it is intended to embrace all variations of alkyl groups disclosed herein, as measured by the number of carbon atoms, the same as if each and every alkyl group were explicitly and individually listed for each usage of the term. When an alkyl residue having a specific number of carbons is named, all geometric isomers having that number of carbons are included, so, for example, "butyl" includes n-butyl, sec-butyl, iso-butyl and t-butyl. Suitable alkyl substituents for heterocycles of polymers described herein e.g., thiophene and selenophene include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl and octyl.

A "heteroalkyl" group or radical indicates an alkyl radical in which one or more hydrogen atoms is replaced by a corresponding one or more halogen atoms, or one or more carbon atoms, CH groups or CH₂ groups is replaced by a corresponding one or more heteroatoms, respectively, the group being replaced having a valence corresponding to that of the heteroatom. So, for example, the heteroalkyl group -CF₃ is a methyl group in which three hydrogen atoms have each been replaced by fluorine, or the heteroalkyl group -CH₂-O-CH₂- is an alkyl group in which a CH₂ group has been replaced by an oxygen atom, or the heteroalkyl group -CH₂-NH-CH₃ is an alkyl group in which a CH radical has been replaced by a nitrogen atom, or the heteroalkyl group -Si(CH₃)₃ is an alkyl group in which a carbon atom has been replaced by a silicon atom. Generally, in this context, the number of replacements is

from 1 to 6 and each "heteroatom" is, independently of the other heteroatoms, O, S, N, Se, P, B, Cl, F, I, Br, Si, Ge or Sn. In the case of halogen substitutions for hydrogen, the number of replacements can be up to 20 hydrogens in the alkyl group.

As used herein, the phrase "heterocycle" means a cyclic compound containing at least two different elements on its ring. A particular subclass of heterocycles includes carbon-based rings wherein one or more of the nodal carbons is replaced with a non-carbon atom. In the specific context of copolymers of this invention, heterocyclic rings are aromatic and the terms heterocycle and heteroaryl are used interchangeably.

An alkyl group, a heteroalkyl group, or a heteroaryl group can be substituted with one or more of nitro, carboxyl, formyl, alkylcarbonyl ($-\text{C}(\text{O})-\text{R}$) and heteroalkylcarbonyl. The alkyl group of an alkylcarbonyl or heteroalkyl of a heteroalkylcarbonyl group can also be substituted with a nitro or carboxyl group.

Copolymers of the invention that can exist as a salt are intended to be covered by the structural representations of the copolymers provided herein. For example, a copolymer in which a substituent R-group of a heteroaryl ring that contains a carboxyl group can exist as a salt depending upon conditions used for isolation of the copolymer.

It should be noted here, that when discussing radical portions of a molecule, such as in the foregoing paragraphs, connecting bonds of groups or radicals or atoms may be omitted in various contexts for the sake of convenience, and the skilled person understands this.

This invention may also be said broadly to be composed of the parts, elements and features referred to or indicated herein, individually or collectively, in their various possible combinations. It is to be understood that those combinations and/or subcombinations and e.g., subranges are described as though each is explicitly described herein. So, for example, in one aspect, the invention includes a block copolymer having a first heterocycle that is thiophene, optionally substituted in one or both of the 3-position and the 4-position, and a second heterocycle that is selenophene, optionally substituted in one or both of the 3-position and the 4-position, wherein an optional substituent is an alkyl group. So a block copolymer made up of thiophene blocks and selenophene blocks in which, for example, in

which each of the selenophene and thiophene rings is substituted at the 3-position with an alkyl group is described as though explicitly described in the foregoing description. Likewise, ranges and subranges are described as though each is explicitly described herein. For example, in formula (6), n is larger than 1 and less than 10,000, values for n include 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, and 24. a range of n from 3 to 24 is thus described as though explicitly described in the foregoing description.

As used herein, the phrase "statistical copolymers" means a polymer composed of two or more chemically distinct monomers which are distributed randomly throughout the polymer chain.

As used herein, the phrase "phase separation" (and variants thereof such as "phase separable") refers to any process by which a substance, initially in a single, substantially homogenous phase, separates into two or more distinct phases.

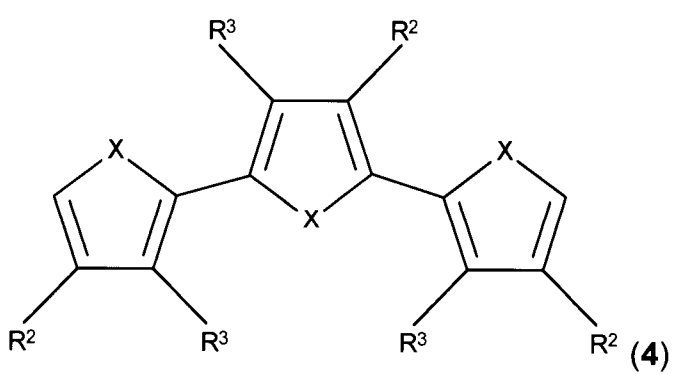
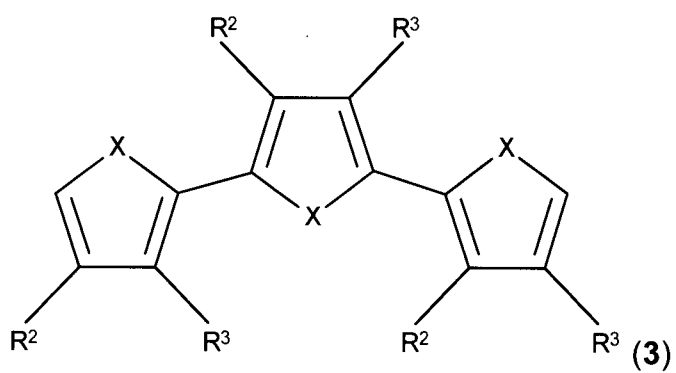
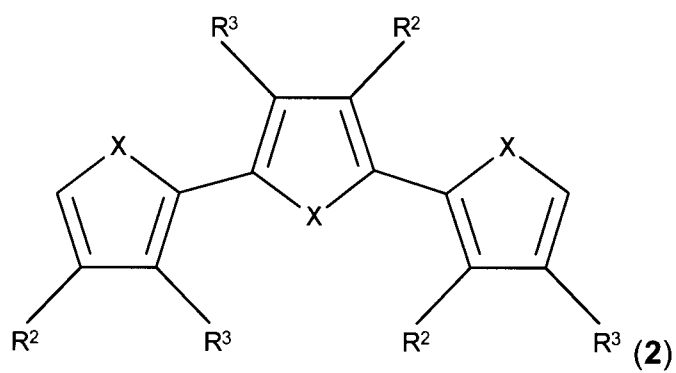
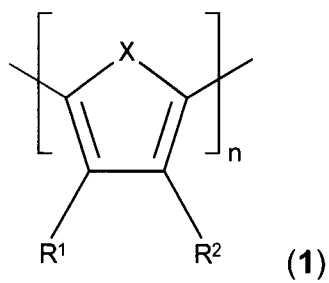
As used herein, the term "phase" means a region of material that has substantially similar composition and structure throughout.

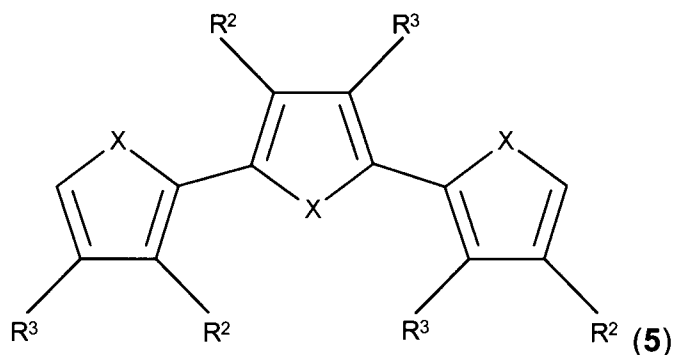
As used herein, the term "associated with" means linked together by means of the electromagnetic force.

As used herein, the term "good electrical communication" means having an energy bandgap between a conduction state and a bound state of an electron that corresponds to the energy of a photon in any one of the infrared, visible, and ultraviolet ranges.

As used herein, the term "conjugated" means a compound having alternating single and multiple bonds. In the case of a block copolymer of the invention disclosed herein, a copolymer is fully conjugated when the backbone of the polymer is substantially fully conjugated from end to end of the backbone.

As used herein, the polymer represented by formula (1) (wherein X is a heteroatom) can have any level of regioregularity. That is to say, it can be composed of a plurality of any combination of the four distinct triads shown in formulae (2)–(5). Due to the possibly asymmetrical nature of the monomer shown by formula (1) (the monomer is asymmetrical when R¹ and R² are chemically distinct), the polymer comprising repeated such monomers can comprise a plurality of any combination of these four distinct triads.





Broadly speaking, herein is disclosed a novel class of block copolymers that are fully conjugated and capable of self-assembly through phase separation. Examples include a novel selenophene-thiophene block copolymer. Also disclosed is

5 a class of composite materials comprising the above mentioned phase-separable fully conjugated block copolymers and nanocrystals, as well as methods for the assembly of the nanocrystals through the phase separation of the polymers. These materials and methods have applications in a variety of electronic devices, particularly optoelectronic devices, even more particularly devices such as diodes,

10 light-emitting diodes, transistors, solar cells, photodiodes and light-emitting transistors as conductive, semi-conductive or light absorbing materials.

Polythiophene is well-studied and known to organize into ordered domains. Polyselenophene is a new conjugated polymer with a narrower gap between the HOMO (highest occupied molecular orbital) level and the LUMO (lowest unoccupied

15 molecular orbital) level than in polythiophene. Both polymers can be synthesized under quasi-living conditions, which allows for the synthesis of distinct block copolymers.

The self-assembly of diblock copolymers is particularly attractive because it is an inexpensive and scalable process that can be rationally designed to produce a

20 stable solid-state composite.⁶ In general, polymers can be designed to undergo phase separation by synthesizing copolymers that contain regions with distinct functional groups, and when combined with nanoparticles, block copolymer self-assembly offers a means to control the organization of nanoparticles within a film.⁶ This strategy has been demonstrated for several coil-coil-type block copolymers

25 including poly(styrene)-b-poly(ethylene propylene), poly(styrene)-b-poly(methylmethacrylate), and poly(styrene)-b-poly(vinyl pyridine).⁶ On the other

hand, this approach has not been tested for rod-rod type copolymers, which includes all classes of conjugated diblock copolymers.

Selenophene-thiophene block copolymers can be used to drive the self-assembly of spherical nanocrystals (NCs) within a conjugated polymer film (**Figure 1**). The resultant composite materials consist of nanofibers of phase-separated conjugated polymer with NCs that are aligned into continuous networks, and preferentially associated with one polymer phase. Photoluminescence quenching experiments demonstrate that this approach leads to films with good electronic communication between the organic and inorganic semiconducting materials.

Self-assembled fibers of selenophene-thiophene block copolymers can be used to align spherical NCs into periodic linear networks. Interestingly, the NCs appear to have a selective affinity for the thiophene phase of the phase-separated block copolymer. Prior art teaches the production of polymer-nanoparticle composites with a controlled hierarchical morphology using solely coil-coil-type block copolymers. Herein is shown that the organization of nanocrystals can be effected in conjugated diblock copolymers as well, which are not coil-coil-type block copolymers, but fall within the category of rod-rod polymers. This opens the door for using conjugated block copolymers to assemble nanoparticles in a rational manner.

In an aspect, the invention includes a phase-separable block copolymer comprising a first fully conjugated homopolymer and a second fully conjugated homopolymer,

wherein said first fully conjugated homopolymer comprises a first monomer,

wherein said first monomer comprises a first heterocycle,

wherein said second fully conjugated homopolymer comprises a second

monomer, and

and wherein said second monomer comprises a second heterocycle

chemically distinct from said first heterocycle.

The first heterocycle can be thiophene, optionally substituted in one or both of the 3-position and the 4-position, the substitutions being independent of each other.

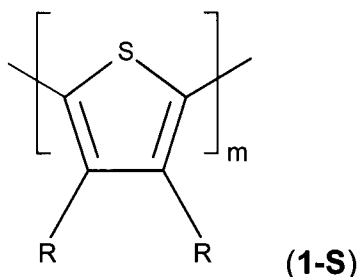
The second heterocycle can be selenophene, optionally substituted in one or both of the 3-position and the 4-position, these substitutions also being independent of each other.

The optional substituents can be selected from the group consisting of nitro, carboxyl, formyl, and alkylcarbonyl, and alkyl optionally substituted with one or more of nitro, carboxyl, formyl, alkylcarbonyl and heteroalkylcarbonyl, or heteroalkyl optionally substituted with one or more of nitro, carboxyl, formyl, and alkylcarbonyl.

5 The first monomer can be selected from the group consisting of unsubstituted thiophene, thiophene that is substituted in the 3-position, thiophene that is substituted in the 4-position, and thiophene that is substituted in both the 3-position and the 4-position.

10 The second monomer can be selected from the group consisting of unsubstituted selenophene, selenophene that is substituted in the 3-position, selenophene that is substituted in the 4-position, and selenophene that is substituted in both the 3-position and the 4-position.

In an aspect, the first fully conjugated homopolymer is shown by formula (1-S)

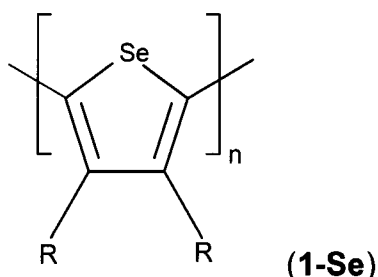


15 wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

20 wherein R¹, R², R³, and R⁴ are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

wherein m is from 2 to 10,000.

In an aspect, the second fully conjugated homopolymer is shown by formula (1-Se)



wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

5 wherein R¹, R², R³, and R⁴ are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

 wherein n is from 2 to 10,000.

 In embodiments, the first fully conjugated homopolymer is poly(3-hexylthiophene) and/or the second fully conjugated homopolymer is poly(3-hexylselenophene).
10

 The molar ratio of 3-hexylthiophene to 3-hexylselenophene can be greater than 1:2000 and less than 2000:1. In various aspects, the molar ratio of 3-hexylthiophene to 3-hexylselenophene is greater than 1:1000 and less than 1000:1, or is greater than 1:500 and less than 500:1, or is greater than 1:200 and less than 200:1,
15 or is greater than 1:100 and less than 100:1, or is greater than 1:50 and less than 50:1, or is greater than 1:10 and less than 10:1, or is greater than 1:5 and less than 5:1, or is between 1:2 and 2:1.

 In a particular aspect of the invention, the molar ratio of 3-hexylthiophene to 3-hexylselenophene is about 1:1 in a phase-separable block copolymer.

20 The invention includes an optoelectronic device containing a copolymer of the invention. Such a device can be a diode, a light-emitting diode, a transistor, a solar cell, a photodiode, or a light-emitting transistor.

 A copolymer-nanocrystal composite of the invention can be the phase-separable block copolymer and a plurality of nanocrystals. In a preferred aspect, a
25 copolymer-nanocrystal composite includes a phase-separable block copolymer of the invention that is phase-separated.

 In another aspect, a copolymer-nanocrystal composite of the invention is a phase-separable block copolymer arranged in nanofibers, and preferably, the plurality of nanocrystals is substantially associated with a phase of said phase-separable block copolymer. The plurality of nanocrystals can be arranged in a
30 substantially periodic linear fashion.

 In an aspect of the invention, the mass ratio of a phase-separable block

copolymer to the plurality of nanocrystals is about 1:1.

A copolymer-nanocrystal composite of the invention preferably has the phase-separable block copolymer in good electrical communication with the plurality of nanocrystals.

5 Such a plurality of nanocrystals of a copolymer-nanocrystal composite can be nanocrystals with a conduction band below a LUMO level of the phase-separable block copolymer and a valence band below a HOMO level of the phase-separable block copolymer.

10 The invention includes a method of arranging a plurality of nanocrystals comprising the steps of

- (i) synthesizing the phase-separable block copolymer of any one of claims 1 to 15;
- (ii) mixing said plurality of nanocrystals with a solution comprising said phase-separable block copolymer; and
- 15 (iii) phase separating said phase-separable block copolymer.

The invention also includes a method of adjusting a set of properties of a phase-separable block copolymer wherein

said phase-separable block copolymer comprises a first fully conjugated homopolymer and a second fully conjugated homopolymer,

20 said first fully conjugated homopolymer comprises a first monomer,
 said first monomer comprises a first heterocycle,
 said second fully conjugated homopolymer comprises a second monomer,
 said second monomer comprises a second heterocycle chemically distinct from said first heterocycle, and

25 said method comprises the steps of

- (i) synthesizing said phase-separable block copolymer; and
- (ii) phase separating said phase-separable block copolymer.

The invention includes a semiconductor composite material containing a block copolymer of the invention in combination with an electron acceptor material.

30 In a preferred aspect, the invention is an optoelectronic device having a power conversion efficiency between 0.1 and 15%, or between 2.7 and 15%, or 2.7 and 13%, or 2.7 and 11%, or 2.7 and 9%, or 2.7 and 7%, or 2.7 and 5%, or at least 2.7%,

or at least 3.0%, or at least 4.0%.

A preferred optoelectronic device includes a semiconductor composite material of the invention formed as a film on a conductive substrate in which the film has an Ra of less than 3 nm and the film is formed directly onto the substrate in
5 direct electrical connection therewith.

The invention includes use of a semiconductor composite material in the formation of a semiconducting film.

Thickness of a film on the substrate can be between 1 nm and 10,000 nm, or between 5 nm and 8,000 nm, or between 5 nm and 5,000 nm, or between 5 nm and
10 2,000 nm, or between 5 nm and 1,000 nm, or between 10 nm and 800 nm or between 10 nm and 500 nm, or between 10 nm and 300 nm, or between 20 nm and 300 nm, or between 40 and 200 nm, or between 20 and 300 nm, or it can be about 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, or 150 nm.

The invention thus also includes a method of manufacturing a semiconductor,
15 the method including steps of:

providing a semiconductor composite material of the invention; and
coating a substrate with the semiconductor composite material.

A method can be of manufacturing a solar cell, that includes:

providing a semiconductor comprising a semiconductor composite material of
20 the invention; and
incorporating the semiconductor into the cell.

The invention includes solar cell comprising (i) a cathode and an anode, (ii) an active layer having a first surface and a second surface disposed between the cathode and the anode, and (iii) a titanium dioxide layer formed to be in electrical
25 contact with one of the first surface and the second surface of the active layer, wherein the active layer comprises a semiconductor composite material of the invention.

Such a solar cell can have power conversion efficiency between 0.1 and 15%, preferably greater than about 2.7%.

30 Described below are examples demonstrating the feasibility of using a block copolymer of the invention in conjunction with an electron acceptor to form a semiconductor composite material. The material can be used, for example, as part of

a photovoltaic device. Examples demonstrate the usefulness of inorganic nanoparticles, including a fullerene derivative (PCBM), as electron acceptors, but others would work as well. A further listing of acceptor materials useful in the present invention is found in Kietzke, "Advances in Organic Solar Cells," Advances in OptoElectronics, Volume 2007, Article ID 40285, published on line and in a Review Article by Cheng et. al. (Chem. Rev. 2009, **109**, 5868-5923). For the purposes of this invention, an "electron acceptor" is defined as any molecule, fullerene, nanoparticle, nanocrystal, quantum dot, or composition that can accept an excited-state electron from the block copolymer. The terms nanoparticles, nanocrystal and quantum dots are used interchangeably. Both fullerenes and CdSe nanoparticles were used in studies described herein, but other materials, such as CdS, CdTe, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, and/or Cd₃P₂ can be used. Other shapes, such as spheres, stars, tetrapods can be used also. The fullerene derivative [6,6]-phenyl C₆₁ butyric acid methyl ester was used in the studies described herein, but other fullerenes and/or their derivatives can be used. Fullerene derivatives of the invention are capable of acting as an electron acceptor and include alkyl ester derivatives, particularly PCBM. Fullerenes of the invention include C₆₀, C₇₀, C₈₄, and derivatives such as ester derivatives e.g., the [6,6]-phenyl C₇₁ butyric acid. Materials that can also be incorporated into e.g., an organic solar cell of the invention include carbon nanotubes and graphene. One of the most likely to be used electron acceptors is the fullerene derivative [6,6]-phenyl C₆₁ butyric acid methyl ester used in Examples 3 and 4.

The inventors have surprisingly found that the power conversion efficiency of a prototype solar cell comprising a block copolymer of the invention does not markedly change with thermal annealing of the polymer as is observed for cells that include P3HT as an electron donor. Even more surprising was the finding that cell performance could be improved by spin-coating a solution of the block copolymer onto the substrate when casting is carried out using a heated solution. It is known that use of such a "fast-dry" process in making a solar cell with P3HT:PCBM leads to lower performance (Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y., High-Efficiency Solution Processable Polymer Photovoltaic Cells by Self-Organization of Polymer Blends. *Nat. Mater.* **2005**, 4, 864-868.) than when

casting is carried out using a solution at e.g., room temperature with subsequent thermal annealing at a substantially higher temperature, and/or with solvent vapor annealing.

Given this disclosure, the skilled person can optimize the combinations of materials, sizes, shapes, etc. to obtain a semiconductor composite material for use in a particular setting.

The following examples are presented to enable those skilled in the art to understand and to practice embodiments of the present disclosure. They should not be considered as a limitation on the scope of the present embodiments, but merely as being illustrative and representative thereof.

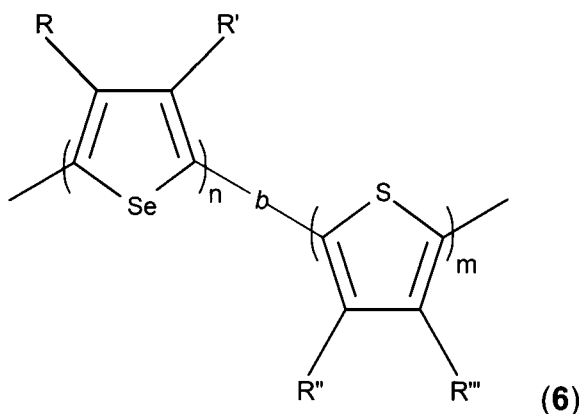
EXAMPLE 1

One embodiment of the present disclosure is exemplified using as an example chemical compounds termed selenophene-thiophene block copolymers.

Thiophene and selenophene monomers with identical side chains were prepared. The thiophene monomers (2,5-dibromo-3-hexylthiophene) were synthesized according to previously reported procedures. The selenophene monomers (2,5-dibromo-3-hexylselenophene) were synthesized by an initial alkylation of 3-iodoselenophene with *n*-hexylmagnesium bromide under Kumada-type coupling conditions followed by isolation and dibromination using *N*-bromosuccinimide (**Figure 2**).

To prepare the block copolymers, the selenophene monomers were activated with *n*-butylmagnesium chloride and treated with [1,3-bis(diphenylphosphino)propane]nickel(II)chloride [Ni(dppp)Cl] to initiate polymerization (**Figure 3**). In a second vessel, the thiophene monomers were activated and added to the polymerization reaction after the selenophene monomers were consumed (10 h). The selenophene:thiophene molar ratio was 1:1, and the catalyst:total monomer molar ratio was 1:100. For control experiments, statistical copolymers and homopolymers [poly(3-hexylthiophene), P3HT, and poly(3-hexylselenophene), P3HS] were prepared under similar conditions.

The general structure of a thiophene-selenophene block copolymer is shown as formula (6):



in which n and m denote the number of selenophenes and thiophenes, respectively.

- 5 Typically, n is larger than 1 and less than 10,000, and m is larger than 1 and less than 10,000. R , R' , R'' , and R''' are independently variable substituents. Common values for n and m , which are independent of each other, are 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, and 24.

- The thiophene and selenophene repeat units have distinct ^1H NMR resonances (6.98 and 7.12 ppm, respectively), and thus, NMR spectroscopy was initially used to determine the structure of the polymers and quantify the monomer incorporation of block and statistical copolymers. Accordingly, the selenophene:thiophene ratios are found to be 57:43 and 45:55 for the block and statistical copolymers, respectively (**Figure 4**). In the statistical copolymer, the aromatic resonances of thiophene and selenophene appear at different chemical shifts when the alternate heterocycle is present at the 5-position. The spectrum of the statistical copolymer was therefore particularly useful for quantifying each combination of units along the backbone. The thiophene-thiophene:thiophene-selenophene: selenophene-selenophene distribution is 29:50:21, confirming the statistical distribution of monomers in the chain. In the block copolymer, the resonance that corresponds to the single selenophene-thiophene linkage was difficult to quantify above the noise in the spectra for this molecular weight range (M_n 7.4 kg/mol). Oligomers were generated using a monomer:catalyst ratio of 5:100 (**Figure 3**).

- 25 To further determine structure, optical studies in chlorobenzene were carried out. The absorption edge of the block copolymer and P3HS are identical (620 nm),

confirming the presence of the long polyselenophene chromophore in the block structure (**Figure 5a**). The absorption edge of the statistical copolymer (600 nm) is positioned between those of P3HT and P3HS, indicating that a combination of thiophene and selenophene constitute the chromophore. The full width at half-
5 maximum of the absorption band of the block copolymer (145 nm) is greater than those of the statistical copolymer (130 nm) and the two homopolymers (P3HT = 123 nm; P3HS = 140 nm). This is consistent with a structure in which the block copolymer contains intact polythiophene and polyselenophene chromophores. The solution fluorescence spectra are also indicative of structure. For reference, P3HT
10 and P3HS emit at 578 and 623 nm, respectively (**Figure 5b**). The block copolymer emission spectrum is dominated by emission from the thiophene block because of this block's greater fluorescence intensity. On the other hand, the statistical copolymer emits weakly at 598 nm, a frequency positioned between the P3HT and P3HS emissions. Taken together, the ^1H NMR and solution optical measurements
15 are consistent with the proposed structures of the polymers.

The solid-state properties of the block copolymer were examined. Films were prepared by spincoating followed by annealing (150°C, 1 h), and the absorbance properties were measured. Interestingly, the absorption profile of the block
20 copolymer possesses shoulders (marked by arrows in **Figure 5c**) that coincide with the π -stacking bands of both P3HT and P3HS. These features indicate association and organization of blocks with corresponding blocks in adjacent chains. This observation stands in contrast to that for the statistical copolymer, which has a nearly featureless absorption profile. The film morphology of the block copolymer was also investigated using atomic force microscopy (AFM). Distinct domains are present in
25 the film (**Figure 6**). This morphology is striking when compared with the statistical copolymer film, which has much smaller domains with a smoother morphology, or when compared with blends of the two pure polymers, which appear unstructured at the nanoscale (**Figure 6**). Taken together, the absorption and AFM data
30 demonstrate that the block copolymer undergoes a significant degree of phase separation in the solid state.

More detailed information was available from dark-field scanning transmission electron microscopy (STEM) measurements. In these unstained images (**Figure 5c**),

bright cylindrical features similar in size to those observed using AFM can be seen. These features represent domains with a high electron scattering ability and are most likely due to selenophene-rich phases. Topographic elemental mapping lends support to this hypothesis, showing that the bright regions are rich in selenium and
5 deficient in sulfur. Conversely, the darker regions are rich in sulfur and deficient in selenium (**Figure 7a**), confirming that the features arise from blocks of distinct heterocycles that preferentially associate in the film. This preference is quite surprising in view of the fact that selenophene and thiophene are so structurally similar.

10 **EXAMPLE 2**

This example describes the use of the block copolymers to drive the assembly of nanocrystals. Selenophene-thiophene block copolymers were synthesized according as described above. Briefly, n-Butylmagnesium chloride (0.14 mL, 2.0 M in THF, 0.28 mmol) was added drop-wise to a solution of 2,5-dibromo-3-
15 hexylselenophene (100 mg, 0.27 mmol) in dry THF (1.5 mL) under a nitrogen atmosphere, refluxed for 1 hour, and transferred to a nitrogen filled flask containing Ni(dppp)Cl₂ (3.0 mg, 5.4 nmol) and refluxed for 5 hours, then 3mL of THF was added and refluxed for 0.5 hour (Solution A). In a separate flask n-butylmagnesium chloride (0.14 mL, 2.0 M in THF, 0.28 mmol) was added to 2,5-dibromo-3-
20 hexylthiophene (87 mg, 0.27 mmol) in dry THF (1.5 mL) and the solution was refluxed for 1 hour (Solution B). Solution A was refluxed for 10 hours at which time Solution B was added drop-wise. The combined mixture was refluxed for an additional 10 hours, then quenched with dilute hydrochloric acid and precipitated into methanol. The precipitated solid was purified by Soxhlet extraction using hexanes,
25 methanol, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep purple solid, (15 mg, 20%, ¹H NMR (CDCl₃, 300 MHz): δ 7.12 (s, 1H), 6.98 (s, 1H), 2.72-2.82 (4H), 1.65-1.72 (4H), 1.25-1.46 (12H), 0.90-0.93 (6H). Mn=4.0 kg/mol, Mw=8.3 kg/mol, PDI = 2.1. The thiophene-selenophene incorporation ratio was determined by ¹H NMR spectroscopy by integrating the
30 aromatic peaks for selenophene (δ = 7.12) and thiophene (δ = 6.98) (**Figure 8**).

The self-assembled structure of polymer-only films was first investigated. Films were prepared by drop casting from chlorobenzene (10 mg/mL) and imaged by

dark-field scanning transmission electron microscopy (STEM). The STEM images (**Figure 9f**) show that polymers form fibers composed of several bright and dark areas, which are several hundreds of nanometers long and 20-80 nanometers thick depending on the number of bright and dark phases within the fiber. Topographic elemental linescan (**Figure 10**) shows that the bright regions are rich in selenium and deficient in sulfur, while the dark regions are rich in sulfur and deficient in selenium. This confirms that heterocycle-specific phase separation occurs in the polymer-only fibers. It also appears that when drop cast from solution, several alternating phases are present within each dry self-assembled fiber (**Figure 9g**).

Block copolymer-NC blends (1:1; w/w) were prepared in chlorobenzene (10 mg/mL) and investigated their morphology after drop casting. Here, a surprising co-self-assembly of NCs with polymer fibers is observed. Numerous new, aligned features can be seen on the nanofibers (**Figure 9a**). A magnified image shows that the new features are NCs that arrange in a linear order onto the polymer fibers (**Figure 9b, c, e**). When comparing the blend with the fibers formed by the block copolymer alone, it is reasonable to assume that the NCs are selectively associated with one of the phases (either selenophene or thiophene), but not both. Magnified STEM images (**Figure 9d and e**) show that the NCs are associated with the darker phase (S-rich phase; red arrows), leaving the brighter phase (Se-rich phase; green arrows) empty. Elemental linescan (**Figure 11**) of the aligned NCs shows that the Cd peaks do not overlap with the broad Se peaks (from the polymer) confirming that the NCs are selectively associated with the sulfur rich phase.

Having determined that selenophene-thiophene block copolymers can be used to self-assemble spherical NCs, the structure of these novel composite materials was investigated. Drop-cast films of block copolymer and block copolymer-NC blends were investigated by wide-angle X-ray scattering (WAXS). The block copolymer film is clearly crystalline, showing two strong diffraction peaks at 2θ angles of 5.64° and 7.30° , corresponding values of 15.49 and 12.14 Å, respectively (**Figure 12a**). The 15.49 Å spacing is likely due to the interlayer stacking (d_{100}) of the hexylthiophene phase (d_{P3HT}). This value is very close to the reported lamellar structure of poly-3-hexylthiophene (P3HT) which has an interlayer spacing of 16.0 ± 0.2 Å. The 12.14 Å spacing is ascribed to the interlayer stacking of the

hexylselenophene phase (dP3HS). Although this interlayer d-spacing is smaller than that which was reported for pristine poly-3-hexylselenophene (P3HS = 15.2 Å), it is consistent in that the d-spacing for P3HS is smaller than that of P3HT. A smaller d-spacing has also been observed in selenophene oligomers. The low intensity peak at 14.55° is likely associated with the (200) diffraction of P3HS block. Due to the relatively long block of P3HS, both (100) and (200) diffraction peaks of the P3HS block are seen. When the block copolymer is blended with NCs, the same two d-spacing peaks are observed. This is important because it shows that NCs do not change polymer crystallization, which is likely the main driving force for the self-assembly of selenophene-thiophene block copolymers.

Conjugated block copolymer/NC composites have potential use as light harvesting materials. This is because both the conjugated polymer and NCs are strong light absorbers and the LUMO level of the polymer is positioned above the conduction band of CdSe while the HOMO level of the polymer is positioned above the valence band of CdSe.⁷ From an energy transfer perspective, photoinduced charge separation would be expected based on the energy level alignment and physical contact of these two materials.

Because photoinduced charge separation would be expected to quench the luminescence of both the polymer and NCs, photoluminescence (PL) quenching experiments were carried out in blended films. Upon illumination at $\lambda = 470\text{nm}$, a film of only NCs emits strongly at $\lambda = 602\text{nm}$. If the NCs are mixed with selenophene-thiophene block copolymers prior to casting however, the $\lambda = 602\text{nm}$ emission is quenched by 72% (**Figure 12b**). Comparing the spectra of the NC-only film with the NC/polymer film clearly shows the efficient PL quenching of NCs, even at relatively low loading of polymer (1.2%; w/w), which indicates efficient excitation energy transfer (**Figure 5b**). It should be pointed out that at 1.2% polymer loading the UV spectra is nearly identical to the NC-only film, which shows that the diminished luminescence is not due to increased absorption (**Figure 13**). Even when different wavelengths (400 nm, 440 nm, 530 nm) were used to excite the NCs within the NC/polymer film, efficient PL quenching is observed under all tested conditions (**Figure 13**).

Quenching experiments were also carried out on NC films that were blended with P3HT and P3HS homopolymers. Here, it was observed that polythiophene is a more efficient quencher of NC emission than polyselenophene (**Figure 14**). It should be noted that polythiophene and polyselenophene have nearly identical HOMO levels, which means that they are energetically equal energy acceptors. Because quenching efficiency is also distance dependent, the fact that polythiophene is a better quencher may therefore be illustrative of the stronger affinity between NCs and polythiophene, which is also consistent with the observation of selective association of the NCs on the sulfur-rich phase of the block copolymer.

In conclusion, poly-(3-hexylselenophene-*block*-3-hexylthiophene)s are an important new class of copolymer because they have broad optical absorption properties with an onset that is red-shifted by 80 nm compared to P3HT, and the ability to phase separate in the solid-state. Until now, phase separation in conjugated polymers has been effected with nonconjugated blocks or pendant groups. Herein is disclosed the discovery that phase separation as well as optical properties can be controlled by the heterocycle in the polymer chain. This represents a distinct type of phase separation that is driven by elemental composition, which simultaneously offers a direct means to control optical properties. Due to this remarkable ability and resultant properties, poly-(3-hexylselenophene-*block*-3-hexylthiophene)s should find utility for fundamental study, such as testing the limits of phase separation, as well as in optoelectronic applications.

EXAMPLE 3: Selenophene-Thiophene: phenyl C₆₁ butyric acid methyl ester (PCBM) devices

The polymer poly(3-hexylselenophene)-*block*-poly(3-hexylthiophene) was synthesized as follows: 2,5-dibromo-3-hexylselenophene monomer (657 mg, 1.76 mmol) was reacted with *i*-propylmagnesium chloride (2.0M, 0.88mL) in dry THF for one hour at room temperature, then transferred to a separate flask containing [1,3-Bis(diphenylphosphino)propane]dichloronickel (Ni(dppp)Cl₂) (19 mg, 0.035 mmol) and the resulting dark purple mixture was heated to 40 °C for 60 minutes. In a separate flask 2,5-dibromo-3-hexylthiophene (574 mg, 1.76 mmol) was likewise activated for 1 hour then transferred dropwise to the polymerization mixture. The polymerization continued over 18 hours then the mixture was precipitated in

methanol, filtered through a Soxhlet thimble and extracted with methanol, hexanes and chloroform. The chloroform fraction was concentrated to retrieve the purified polymers.

A typical solar cell device is fabricated and tested as follows. Devices were fabricated on commercial indium tin oxide (ITO) substrates (Colorado Concept Coatings) that had a sheet resistance of $\sim 10 \Omega/\square$. These substrates were cleaned in aqueous detergent, deionized (DI) water, acetone and methanol, and subsequently treated in an oxygen-plasma cleaner for 5 minutes to remove any residue and improve charge injection. Next, poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP Al 4083) was coated onto the substrates at 3000 rpm and annealed in air at 130 °C for 15 min. After annealing, substrates were transferred into a nitrogen-filled glove box, where a poly(3-hexylselenophene)-*block*-poly(3-hexylthiophene):[6,6]-phenyl C₆₁ butyric acid methyl ester (P3HS-*b*-P3HT:PCBM; 1:0.8 wt. ratio) blend was coated at 500 rpm followed by annealing (See Table 1). [6,6]-phenyl C₆₁ butyric acid methyl ester is a fullerene that was purchased from American Dye Source. Other fullerenes can be used in this device, including, but not limited to C₆₀, C₇₀, C₈₄, or [6,6]-phenyl C₇₁ butyric acid methyl ester. Carbon nanotubes or graphene may also be blended with P3HS-*b*-P3HT and used in this device. Finally, a 1 nm LiF layer and a 100 nm Al anode was thermally deposited through shadow masks at $\sim 10^{-6}$ torr. Typical device area, as defined by the area of circular Al anode, is 7 mm². A schematical of a device structure is given (**Figure 15**). I-V characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm². The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. External quantum efficiency (EQE) spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Standards and Technology.

Typical I-V curves, EQE spectra and device output characteristics are given below (**Figure 16**; **Figure 17**; Table 1). The I-V curves show that these devices produce a photocurrent upon irradiation under simulated solar conditions. Several parameters were optimized including annealing time and temperature. The highest repeatable efficiency obtained so far is 2.7%. High efficiency of a polymer can be

attained with purification by extraction and column chromatography to remove residual metal catalysts. Devices containing the polymer should be annealed at 100°C for 10 minutes. Further optimization of P3HS-*b*-P3HT polymer structure including molecular weight and block ratio should improve this efficiency.

5 **Table 1:** Summary of P3HS-*b*-P3HT:PCBM device characteristics.

Annealing Temperature	Annealing Time	Jsc (mA/cm ²)	Voc (V)	FF	PCE (η)
None	None	7.03	0.56	65.29 %	2.57 %
100 °C	10 min	7.47	0.58	62.50 %	2.71 %

EXAMPLE 4: Solar Cells comprised of Selenophene-Thiophenes with Stable, Spontaneously Formed Nanostructures

Details of the fabrication of a device of the invention is described at the end of this example. Generally, P3HS-*b*-P3HT films were spin-coated from hot solution using a "fast dry" process, and this was followed by heating at 80°C until films were dried as determined by the color change from solution to film, about 30 seconds. This annealing treatment was carried out on a hot plate in glove box before transferring the samples into an evaporator, while post-annealing was carried out after depositing top electrodes. A 0.8 nm LiF layer and a 100 nm thick Al anode was thermally deposited through a shadow mask at $\sim 10^{-6}$ torr. The device area was about 0.07 cm² as defined by the area of circular Al anode. I-V characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm². The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Standards and Technology.

For P3HS-*b*-P3HT, the annealed devices only slightly improved from initial performance (from 2.69% without annealing to 2.76% with annealing, **Figure 18**). AFM measurements show that P3HS-*b*-P3HT:PCBM has a nearly identical fiber-like morphology with or without annealing (**Figure 19a, d**). The fast-dry process

employed, in which the active layers were spun cast from 80°C solutions, was followed by drying quickly at these temperatures, which is different than thermal or solvent annealing. The surface features of the P3HS-*b*-P3HT:PCBM active layer consists of lamella fibers that are 10-20 nm apart, a distance that is roughly equal to the exciton diffusion length. Fiber-like structures have been considered important to improve phase-separation between the donor and acceptor domains, thereby enhancing charge transport and separation.

Having determined that annealing does not significantly change the morphology or performance of P3HS-*b*-P3HT:PCBM device, thermal stability of the system was investigated. Finished devices were annealed, referred to here as "post-annealing", and power conversion efficiency was determined as a function of both time and temperature. Post-annealing and device testing were conducted in a nitrogen-filled glove box. The P3HS-*b*-P3HT:PCBM devices were found to be more robust to the high temperature post-annealing process (**Figure 20**). After increasing the post-annealing temperature to 100°C, the P3HS-*b*-P3HT:PCBM devices retained 83 % of their initial efficiencies, while the performance of P3HT:PCBM devices was found to drop by more than 50%.

The robustness of P3HS-*b*-P3HT devices was also studied during post-annealing at fixed temperature as a function of time (**Figure 21**). P3HT devices lost over 25 % PCE after post-annealing for 30 minutes at 80°C, while P3HS-*b*-P3HT:PCBM devices remained above 90 % of the initial operating efficiency under the same experimental conditions.

It was also observed that the degradation tendency of the P3HT:P3HS:PCBM (physical mixture of three materials) was very similar to that of P3HT:PCBM, showing that the block copolymer architecture is important for thermal stability. The I-V curves show that the decline of current is slowed down in P3HS-*b*-P3HT:PCBM device (**Figure 22**), which can likely be attributed to a stabilized donor-acceptor interface and is consistent with AFM measurements.

The results thus demonstrate that a stable nanostructure is formed by the block copolymer, as devices using P3HS-*b*-P3HT were found to be more robust than homopolymers or mixtures.

Device Fabrication

P3HT, P3HS or P3HS-*b*-P3HT and PCBM were mixed in 1,2-dichlorobenzene (15 mg/mL total polymer:12 mg/mL PCBM) and stirred for 16 hours at 80°C to completely dissolve the solids. Devices were fabricated on commercial indium tin oxide (ITO) substrates (Colorado Concept Coatings) that had a sheet resistance of ~10 $\Omega/\square$. These substrates were cleaned in aqueous detergent, deionized (DI) water, acetone and menthol, and subsequently treated in an oxygen-plasma cleaner for 5 minutes. Next, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP Al 4083) was coated onto the substrates at 3000 rpm and the PEDOT:PSS-coated substrates were annealed in air at 130°C for 15 minutes. After annealing, the substrates were transferred into a nitrogen-filled glove box, where polymer:PCBM blends were coated at 800 rpm. After spin-coating, P3HT samples were immediately transferred into closed petri-dishes and slow dried at room temperature (a vapor annealing process; the optimized condition). For P3HS, P3HS-*b*-P3HT and P3HS:P3HT samples, films were spin-coated from hot solutions followed by heating at 80°C until the films were dry (determined by the color change from solution to film, ~30 seconds). This annealing treatment was carried out on a hot plate in glove box before transferring the samples into an evaporation chamber. A 0.8 nm LiF layer and a 100 nm thick Al anode was thermally deposited through a shadow mask at $\sim 10^{-6}$ torr. The device area is 0.07 cm² as defined by the area of circular Al anode. Post-annealing was carried out after depositing this top electrode. I-V characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5 G conditions with a power intensity of 100 mW/cm². The mismatch of simulator spectrum was calibrated using a Si diode with a KG-5 filter. EQE spectra were recorded and compared with a Si reference cell that is traceable to the National Institute of Standards and Technology. The thickness of active layer is ~150 nm for all devices, determined by AFM. Single carrier devices were fabricated in the same manner as photodiode devices except the LiF/Al cathode was replaced by a Au cathode. I-V characteristics of the single carrier devices were measured under dark conditions and mobility was estimated from the Mott-Gurney law.

EXAMPLE 5: Selenophene-Thiophene: CdSe nanocrystal devices

CdSe nanorods were synthesized by the following procedure which was adapted from the literature.¹⁸ CdO (0.6420 g, 5 mmol) and thiodipropionic acid (TDPA) (2.79 g, 10 mmol) with 2 g of trioctylphosphine oxide (TOPO) were loaded into a reaction flask and then heated under argon flow. The mixture turned optically clear at around 300 °C. After the solution was kept at this temperature for 5-10 min, it was allowed to cool to room temperatures under N₂ flow. A solid product (Cd-TDPA) was obtained and was removed from the reaction flask. An aged (for at least 24 hours) and unpurified Cd-TDPA complex (1.71g, 1.6 mmol of Cd) and 2.28 g TOPO were loaded into the reaction flask and heated to 300°C under N₂ flow. After the solution turned clear, the temperature was increased to 320°C. In glove box, Se-TBP (0.253 g with 25% Se in mass, 0.8 mmol of Se) was mixed with 1.447 g TOPO and 0.3 g toluene to obtain the injection solution. This solution was then loaded into a 5 ml syringe and injected into the reaction flask at 320°C. After the injection, the temperature of the reaction mixture was decreased and held at 250°C for 35 min. The resultant CdSe nanorods were washed four times with a mixture of toluene and ethanol to remove excess capping ligand, and the remaining phosphonic acid ligands were exchanged with pyridine by heating the particles in pyridine overnight at 107 °C. Pyridine-treated particles were recovered by precipitation with hexane and dissolved in a 9:1 mixture of chloroform and pyridine at a concentration of 30mg/mL. The resulting solution was sonicated for 1 h and filtered through a 0.45 µm PTFE filter.

A typical solar cells device is fabricated and tested as follows. Devices were fabricated on commercial indium tin oxide (ITO) substrates (Colorado Concept Coatings) that had a sheet resistance of ~10 Ω/□. These substrates were cleaned in aqueous detergent, deionized (DI) water, acetone and menthol, and subsequently treated in an oxygen-plasma cleaner for 5 minutes to remove any residue and improve charge injection. Next, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) (Clevios P VP AI 4083) was coated onto the substrates at 3000 rpm and annealed in air at 130 °C for 15 min. After annealing, substrates were transferred into a nitrogen-filled glove box. P3HS-*b*-P3HT and CdSe quantum rods are pre-dissolved in different solvents, and then mixed completely at a specified ratio

for spin-coating. After dried, a 1 nm LiF layer and a 100 nm Al anode was thermally deposited through shadow masks at $\sim 10^{-6}$ torr. Typical device area is 7 mm². Output characteristics were measured as described in Example 3. Typical I-V curves, EQE spectra and device output characteristics are given below (**Figure 23**; **Figure 24**;

5 **Table 2**).

Table 2: Summary of P3HS-*b*-P3HT:CdSe device characteristics.

P3HS_b_P3HT:CdSe	Jsc	Voc	FF	PCE
wt%	mA/cm ²	V	%	%
5:95	0.11	0.36	31.91	0.013
11:89	0.12	0.48	37.56	0.022
20:80	0.07	0.52	39.46	0.014
33:67	0.06	0.50	36.66	0.011

The specific embodiments described above have been shown by way of example, and it should be understood that these embodiments may be susceptible to various modifications and alternative forms. It should be further understood that the claims are not intended to be limited to the particular forms disclosed, but rather to cover all modifications, equivalents, and alternatives falling within the spirit and scope of this disclosure.

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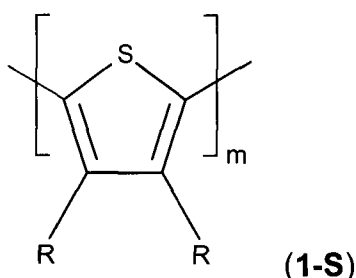
THEREFORE WHAT IS CLAIMED IS:

1. A phase-separable block copolymer comprising a first fully conjugated homopolymer and a second fully conjugated homopolymer,
wherein said first fully conjugated homopolymer comprises a first monomer,
wherein said first monomer comprises a first heterocycle,
wherein said second fully conjugated homopolymer comprises a second monomer,
and wherein said second monomer comprises a second heterocycle chemically distinct from said first heterocycle.
2. The phase-separable block copolymer of claim 1, wherein said first heterocycle is thiophene, optionally substituted in one or both of the 3-position and the 4-position, said substitutions being independent of each other, and wherein said second heterocycle is selenophene, optionally substituted in one or both of the 3-position and the 4-position, said substitutions being independent of each other.
3. The phase-separable block copolymer of claim 2, wherein the optional substituents are selected from the group consisting of nitro, carboxyl, formyl, and alkylcarbonyl, and alkyl optionally substituted with one or more of nitro, carboxyl, formyl, alkylcarbonyl and heteroalkylcarbonyl, or heteroalkyl optionally substituted with one or more of nitro, carboxyl, formyl, and alkylcarbonyl.
4. The phase-separable block copolymer of claim 1 wherein said first monomer is selected from the group consisting of unsubstituted thiophene, thiophene that is substituted in the 3-position, thiophene that is substituted in the 4-position, and thiophene that is substituted in both the 3-position and the 4-position.
5. The phase-separable block copolymer of claim 1 wherein said second monomer is selected from the group consisting of unsubstituted selenophene, selenophene that is substituted in the 3-position, selenophene that is substituted in the 4-position, and selenophene that is substituted in both the 3-position and the 4-position.
6. The phase-separable block copolymer of claim 1
wherein said first monomer of said first fully conjugated homopolymer is selected from the group consisting of unsubstituted thiophene, thiophene that is

substituted in the 3-position, thiophene that is substituted in the 4-position, and thiophene that is substituted in both the 3-position and the 4-position;

and wherein said second monomer of said second fully conjugated homopolymer is selected from the group consisting of unsubstituted selenophene, selenophene that is substituted in the 3-position, selenophene that is substituted in the 4-position, and selenophene that is substituted in both the 3-position and the 4-position.

7. The phase-separable block copolymer of claim 1 wherein said first fully conjugated homopolymer is shown by formula (1-S)

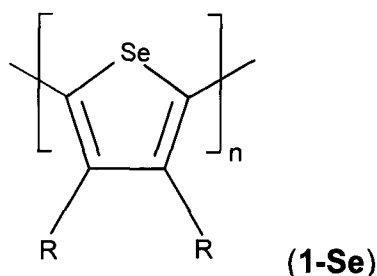


wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

wherein R¹, R², R³, and R⁴ are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

wherein m is from 2 to 10,000.

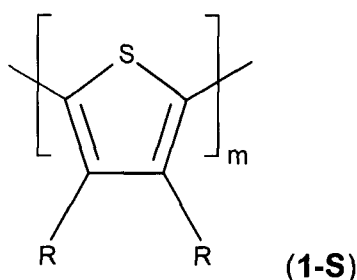
8. The phase-separable block copolymer of claim 1 wherein said second fully conjugated homopolymer is shown by formula (1-Se)



wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

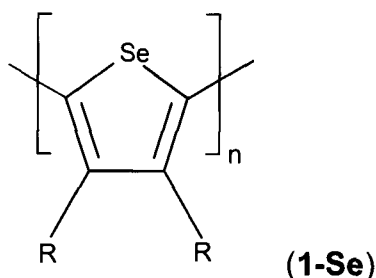
wherein R^1 , R^2 , R^3 , and R^4 are each independently hydrocarbons that contain 1 to 100 carbon atoms; and
 wherein n is from 2 to 10,000.

9. The phase-separable block copolymer of claim 1 wherein said first fully conjugated homopolymer is shown by formula (1-S)



wherein each R is independently selected from the group consisting of H, NO_2 , NH_2 , COOH , CHO , F, Cl, Br, I, BH_2 , OH, SH, SeH, OR^1 , SR^2 , SeR^3 , COR^4 , a functional group, and a hydrocarbon chain that is 1 to 100 carbons in length that may or may not have hydrocarbon and heteroatomic substituents;

wherein said second fully conjugated homopolymer is shown by formula (1-Se)



wherein each R is independently selected from the group consisting of H, NO_2 , NH_2 , COOH , CHO , F, Cl, Br, I, BH_2 , OH, SH, SeH, $\text{OR}^{1'}$, $\text{SR}^{2'}$, $\text{SeR}^{3'}$, $\text{COR}^{4'}$, a functional group, and a hydrocarbon chain that is 1 to 100 carbons in length that may or may not have hydrocarbon and heteroatomic substituents;

wherein R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

wherein m and n are, independently from 2 to 100,000.

10. The phase-separable block copolymer of any one of claims 1 and 9 wherein said first fully conjugated homopolymer is poly(3-hexylthiophene).

11. The phase-separable block copolymer of any one of claims 1 and 9 wherein said second fully conjugated homopolymer is poly(3-hexylselenophene).

12. The phase-separable block copolymer of claim 9 wherein said first fully conjugated homopolymer is poly(3-hexylthiophene), and wherein said second fully conjugated homopolymer is poly(3-hexylselenophene).
13. The phase-separable block copolymer of claim 12 wherein the molar ratio of 3-hexylthiophene to 3-hexylselenophene is greater than 1:2000 and less than 2000:1.
14. The phase-separable block copolymer of claim 12 wherein the molar ratio of 3-hexylthiophene to 3-hexylselenophene is greater than 1:1000 and less than 1000:1, or is greater than 1:500 and less than 500:1, or is greater than 1:200 and less than 200:1, or is greater than 1:100 and less than 100:1, or is greater than 1:50 and less than 50:1, or is greater than 1:10 and less than 10:1, or is greater than 1:5 and less than 5:1, or is between 1:2 and 2:1.
15. The phase-separable block copolymer of claim 12 wherein the molar ratio of 3-hexylthiophene to 3-hexylselenophene is about 1:1.
16. An optoelectronic device comprising the phase-separable block copolymer of any one of claims 1 to 15.
17. The optoelectronic device of claim 16 wherein said optoelectronic device is selected from the group consisting of a diode, a light-emitting diode, a transistor, a solar cell, a photodiode, and a light-emitting transistor.
18. A copolymer-nanocrystal composite comprising the phase-separable block copolymer of any one of claims 1 to 15 and a plurality of nanocrystals.
19. The copolymer-nanocrystal composite of claim 18 wherein said phase-separable block copolymer is phase-separated.
20. The copolymer-nanocrystal composite of claim 18 wherein said copolymer-nanocrystal composite is crystalline.
21. The copolymer-nanocrystal composite of claim 19 wherein said phase-separable block copolymer is arranged in nanofibers.
22. The copolymer-nanocrystal composite of any one of claims 18 to 21 wherein said plurality of nanocrystals is substantially associated with a phase of said phase-separable block copolymer.

23. The copolymer-nanocrystal composite of any one of claims 18 to 22 wherein said plurality of nanocrystals is substantially arranged.
24. The copolymer-nanocrystal composite of claim 23 wherein said plurality of nanocrystals is arranged in a substantially periodic linear fashion.
25. The copolymer-nanocrystal composite of any one of claims 18 to 24 wherein said plurality of nanocrystals comprises substantially spherical nanocrystals.
26. The copolymer-nanocrystal composite of any one of claims 18 to 25 wherein said plurality of nanocrystals comprises cadmium-selenium nanocrystals.
27. The copolymer-nanocrystal composite of any one of claims 18 to 25 wherein said plurality of nanocrystals comprises an allotrope of carbon.
28. The copolymer-nanocrystal composite of any one of claims 18 to 25 wherein said plurality of nanocrystals comprises compounds selected from the group consisting of CdSe, CdTe, CdS, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, Cd₃P₂, C₆₀, phenyl-C₆₁-butyric acid methyl ester, C₇₀, phenyl-C₇₁-butyric acid methyl ester, C₈₄, carbon nanotubes and graphene.
29. The copolymer-nanocrystal composite of any one of claims 18 to 25 wherein the mass ratio of said phase-separable block copolymer to said plurality of nanocrystals is about 1:1.
30. The copolymer-nanocrystal composite of any one of claims 18 to 29 wherein said phase-separable block copolymer is in good electrical communication with said plurality of nanocrystals.
31. The copolymer-nanocrystal composite of claim 30 wherein said plurality of nanocrystals comprises nanocrystals with a conduction band below a LUMO level of said phase-separable block copolymer and a valence band below a HOMO level of said phase-separable block copolymer.
32. An optoelectronic device comprising the copolymer-nanocrystal composite of any one of claims 18 to 31.
33. The optoelectronic device of claim 32 wherein said optoelectronic device is selected from the group consisting of a diode, a light-emitting diode, a transistor, a photodiode, and a light-emitting transistor.

34. A method of arranging a plurality of nanocrystals comprising the steps of
- (i) synthesizing the phase-separable block copolymer of any one of claims 1 to 15;
 - (ii) mixing said plurality of nanocrystals with a solution comprising said phase-separable block copolymer; and
 - (iii) phase separating said phase-separable block copolymer.
35. The method of claim 34 wherein the mass ratio of said phase-separable block copolymer to said plurality of nanocrystals is about 1:1.
36. The method of any one of claims 34 and 35 wherein said plurality of nanocrystals comprises substantially spherical nanocrystals.
37. The method of any one of claims 34 to 36 wherein said phase-separable block copolymer is in good electrical communication with said plurality of nanocrystals.
38. The method of claim 37 wherein said plurality of nanocrystals comprises nanocrystals with a conduction band below a LUMO level of said phase-separable block copolymer and a valence band below a HOMO level of said phase-separable block copolymer.
39. The method of any one of claims 34 to 38 wherein said plurality of nanocrystals comprises cadmium-selenium nanocrystals.
40. The method of any one of claims 34 to 38 wherein said plurality of nanocrystals comprises an allotrope of carbon.
41. The method of any one of claims 34 to 38 wherein said plurality of nanocrystals comprises nanocrystals selected from the group consisting of CdSe, CdTe, CdS, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, Cd₃P₂, C₆₀, Phenyl-C₆₁-butyric acid methyl ester, C₇₀, Phenyl-C₇₁-butyric acid methyl ester, C₈₄, carbon nanotubes, and graphene.
42. A method of adjusting a set of properties of a phase-separable block copolymer wherein
- said phase-separable block copolymer comprises a first fully conjugated homopolymer and a second fully conjugated homopolymer,
 - said first fully conjugated homopolymer comprises a first monomer,

said first monomer comprises a first heterocycle,
said second fully conjugated homopolymer comprises a second monomer,
said second monomer comprises a second heterocycle chemically distinct
from said first heterocycle, and
said method comprising the steps of
(i) synthesizing said phase-separable block copolymer; and
(ii) phase separating said phase-separable block copolymer.

43. The method of claim 42 wherein said first monomer is selected from the group consisting of unsubstituted thiophene, thiophene that is substituted in the 3-position, thiophene that is substituted in the 4-position, and thiophene that is substituted in both the 3-position and the 4-position.

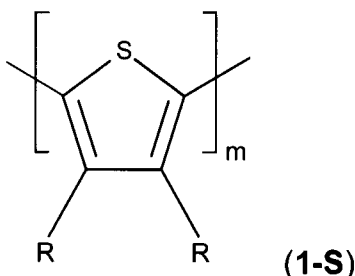
44. The method of claim 42 wherein said second monomer is selected from the group consisting of unsubstituted selenophene, selenophene that is substituted in the 3-position, selenophene that is substituted in the 4-position, and selenophene that is substituted in both the 3-position and the 4-position.

45. The method of claim 42 wherein:

said first monomer is selected from the group consisting of unsubstituted thiophene, thiophene that is substituted in the 3-position, thiophene that is substituted in the 4-position, and thiophene that is substituted in both the 3-position and the 4-position; and

said second monomer is selected from the group consisting of unsubstituted selenophene, selenophene that is substituted in the 3-position, selenophene that is substituted in the 4-position, and selenophene that is substituted in both the 3-position and the 4-position.

46. The method of claim 42 wherein said first fully conjugated homopolymer is shown by formula (1-S)



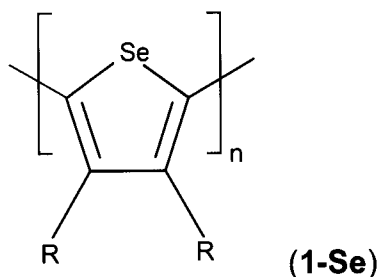
wherein each R is independently selected from the group consisting of H,

NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

wherein R¹, R², R³, and R⁴ are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

wherein m is from 2 to 100,000.

47. The method of claim 42 wherein said second fully conjugated homopolymer is shown by formula (1-Se)

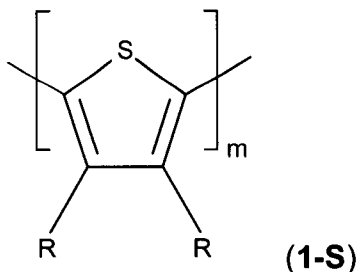


wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

wherein R¹, R², R³, and R⁴ are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

wherein n is from 2 to 100,000.

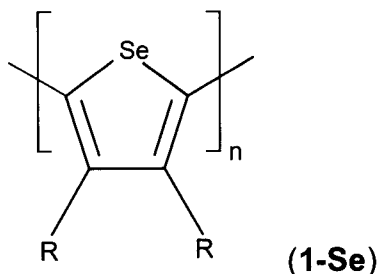
48. The method of claim 42 wherein said first fully conjugated homopolymer is shown by formula (1-S)



wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR¹, SR², SeR³, COR⁴, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents;

wherein said second fully conjugated homopolymer is shown by formula (1-

Se)



wherein each R is independently selected from the group consisting of H, NO₂, NH₂, COOH, CHO, F, Cl, Br, I, BH₂, OH, SH, SeH, OR^{1'}, SR^{2'}, SeR^{3'}, COR^{4'}, a functional group, and a hydrocarbon chain that is 1 to 100 carbon atoms in length that may or may not have hydrocarbon and heteroatomic substituents; and

wherein R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} are each independently hydrocarbons that contain 1 to 100 carbon atoms; and

wherein m and n are, independently from 2 to 100,000.

49. The method of any one of claims 45 and 48 wherein said first fully conjugated homopolymer is poly(3-hexylthiophene).

50. The method of any one of claims 42 and 48 wherein said second fully conjugated homopolymer is poly(3-hexylselenophene).

51. The method of claim 48 where said first fully conjugated homopolymer is poly(3-hexylthiophene) and said second fully conjugated homopolymer is poly(3-hexylselenophene).

52. The method of claim 51 wherein the molar ratio of 3-hexylthiophene to 3-hexylselenophene is greater than 1:200 and less than 200:1.

53. The method of claim 51 wherein the molar ratio of 3-hexylthiophene to 3-hexylselenophene is about 1:1.

54. The method of claim 42 wherein said set of properties comprises morphological properties.

55. The method of claim 42 wherein said set of properties comprises optical properties.

56. A semiconductor composite material comprising a block copolymer as defined by any one of claims 1 to 15 in combination with an electron acceptor material.

57. The semiconductor composite material of claim 56 wherein the block copolymer comprises the block copolymer defined by any one of claims 12 to 15.
58. The semiconductor composite material of claim 57, wherein the block copolymer comprises the block copolymer defined by claim 13.
59. The semiconductor composite material of claim 58, wherein the block copolymer comprises the block copolymer defined by claim 14.
60. The semiconductor composite material of claim 58, wherein the block copolymer comprises the block copolymer defined by claim 15.
61. The semiconductor composite material of any one of claims 56 to 60, wherein the acceptor material comprises a plurality of nanocrystals.
62. The semiconductor composite material of claim 61 wherein said phase-separable block copolymer is phase-separated.
63. The semiconductor composite material of claim 61 wherein the semiconductor composite material is crystalline.
64. The semiconductor composite material of claim 62 wherein said phase-separable block copolymer is arranged in nanofibers.
65. The semiconductor composite material of any one of claims 61 to 64 wherein said plurality of nanocrystals is substantially associated with a phase of the semiconductor composite material.
66. The semiconductor composite material of any one of claims 61 to 65 wherein said plurality of nanocrystals is arranged in a substantially regular or irregular array.
67. The semiconductor composite material of claim 66 wherein said array is a substantially periodic linear arrangement.
68. The semiconductor composite material of any one of claims 61 to 67 wherein the nanocrystals are substantially spherical nanocrystals.
69. The semiconductor composite material of any one of claims 61 to 68 wherein the nanocrystals comprise cadmium-selenium.
70. The semiconductor composite material of any one of claims 61 to 68

wherein said nanocrystals comprise an allotrope of carbon.

71. The semiconductor composite material of any one of claims 61 to 68 wherein the nanocrystals comprise compounds selected from the group consisting of CdSe, CdTe, CdS, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, and Cd₃P₂.

72. The semiconductor composite material of claim 70 wherein the nanocrystals comprise a compound selected from the group consisting of C₆₀, phenyl-C₆₁-butyric acid methyl ester, C₇₀, phenyl-C₇₁-butyric acid methyl ester, C₈₄, carbon nanotubes and graphene.

73. The semiconductor composite material of any one of claims 61 to 72 wherein the mass ratio of said phase-separable block copolymer to said plurality of nanocrystals is about 1:1.

74. The semiconductor composite material of any one of claims 61 to 73 wherein said phase-separable block copolymer is in electrical contact with said plurality of nanocrystals.

75. The semiconductor composite material of claim 74 wherein said plurality of nanocrystals comprises nanocrystals with a conduction band below a LUMO level of said phase-separable block copolymer and a valence band below a HOMO level of said phase-separable block copolymer.

76. An optoelectronic device as defined by claim 17, wherein the device is a solar cell.

77. An optoelectronic device comprising the semiconductor composite material of any one of claims 61 to 75.

78. The optoelectronic device of claim 77, wherein the device has an efficiency between 0.1 and 15%

79. The optoelectronic device of claim 78, wherein the device has an efficiency greater than about 2.7%.

80. An optoelectronic device comprising the semiconductor composite material of claim 56 formed on a substrate and wherein the film has an Ra of less than 3 nm.

81. The device of claim 80, wherein the film comprises fibers of the block

copolymer having an average thickness of from 5 to 500 nm.

82. The device of claim 80 or 81, wherein the device is a solar cell.

83. The device of any one of claims 80 to 82, wherein the electron acceptor material comprises a fullerene, a fullerene derivative, a nanoparticle, nanocrystal, quantum dot, or any combination thereof.

84. The device of claim 83, wherein the electron acceptor material comprises a quantum dot selected from the group consisting of CdSe, CdTe, CdS, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, Cd₃P₂, or any combination of any of the foregoing.

85. The device of any one of claims 82 to 84, wherein the solar cell has a power conversion efficiency of at least 2.7% when exposed to simulated sunlight of an intensity of 1 Sun under AM1.5 G conditions.

86. The device of any one of claims 80 to 85, wherein the film has an average thickness of between 5 and 50 nm.

87. The device of claim 86, wherein the film has an average thickness of between 10 and 20 nm.

88. The device of any one of claims 80 to 87, wherein the film has a nanomorphology that is thermally stable between 25°C and 350°C.

89. The device of claim 88, wherein said nanomorphology is stable at about 80°C.

90. Use of a semiconductor composite material as defined by any one of claims 61 to 73, in the formation of a semiconducting film.

91. Use as defined by claim 90, wherein the film is formed directly to a substrate.

92. Use as defined by claim 90 or 91, wherein the thickness of the film on the substrate is between 1 nm and 10,000 nm, or between 5 nm and 8,000 nm, or between 5 nm and 5,000 nm, or between 5 nm and 2,000 nm, or between 5 nm and 1,000 nm, or between 10 nm and 800 nm or between 10 nm and 500 nm, or between 10 nm and 300 nm, or between 20 nm and 300 nm, or between 40 and 200 nm, or between 20 and 300 nm.

93. Use as defined by claim 92, wherein the substrate comprises a conductive

material or transparent layer.

94. Use as defined by claim 93, wherein said conductive material is a semiconductor layer, a metal, indium tin oxide and/or the transparent layer is a plastic.

95. Use as defined by any one of claims 91 to 94, wherein the film is formed on the substrate by spin-coating, drop casting, doctor blading, ink jet printing, evaporation, or any other method or combination of methods used to deposit matter.

96. Use as defined by any one of claims 90 to 95, wherein the use includes incorporating the composite material into a semiconductor layer for a photovoltaic device.

97. Use as defined by claim 96 wherein the device is a solar cell.

98. A method of manufacturing a semiconductor, the method comprising the steps of:

providing a semiconductor composite material as defined by any one of claims 61 to 75; and
coating a substrate with the semiconductor composite material.

99. A method of manufacturing a solar cell, the method comprising the steps of:
providing a semiconductor comprising a semiconductor composite material as defined by any one of claims 61 to 75; and
incorporating the semiconductor into the cell.

100. The method of claim 99, wherein the step of providing a semiconductor includes coating a substrate with the semiconductor composite material as defined by any one of claims 60 to 74.

101. A method of manufacturing a solar cell, the method comprising the steps of:
providing a semiconductor comprising a semiconductor composite material as defined by any one of claims 80 to 88; and
incorporating the semiconductor into the cell.

102. A solar cell comprising (i) a cathode and an anode, (ii) an active layer having a first surface and a second surface disposed between the cathode and the anode, and (iii) a titanium dioxide layer formed to be in electrical contact with one of the

first surface and the second surface of the active layer, wherein the active layer comprises a semiconductor composite material as defined by any one of claims 61 to 75.

103. The solar cell of claim 102, wherein the cell has an efficiency between 0.1 and 15%.

104. The solar cell of claim 103, wherein the cell has an efficiency greater than about 2.7%.

105. A method for making a photovoltaic device, the method comprising:

(i) providing a solution of a block copolymer as defined by any of claims 1 to 14; and

(ii) applying the solution to a substrate;

wherein the temperature of at least one of the solution and substrate is controlled to be at least 40°C during step (ii).

106. The method of claim 105, wherein said temperature of at least one of the solution and substrate is controlled to be in the range from 60°C to 100°C.

107. The method of claim 105 or 106, wherein the temperature of the solution is controlled to be in the range from 60°C to 100°C during step (ii).

108. The method of claim 107, wherein said temperature of the solution is controlled to be in the range from 70°C to 90°C during step (ii).

109. The method of any one of claims 105 to 108, wherein the temperature of the substrate is controlled to be at least 40°C during step (ii).

110. The method of any one of claims 105 to 109, wherein the temperature of the solution is controlled and/or the temperature of the substrate is controlled to form a film on the substrate, the film comprising fibers of the block copolymer having an average thickness of from 5 to 500 nm.

111. The method of claim 110, wherein the temperature of the solution is further controlled and/or the temperature of the substrate is further controlled to form a film having an Ra of less than 3 nm.

112. The method of claim 110 or claim 111, wherein applying the solution comprises forming the film on the substrate by spin-coating, drop casting, doctor

blading, ink jet printing, evaporation, or combination of any of the foregoing methods.

113. The method of claim 110, 111 or 112, further comprising drying the film formed in step (ii) at a temperature equal to or greater than the temperature of step (i).

114. The method of claim 113, wherein the film is maintained at a temperature greater than or equal to the temperature of step (i) throughout step (ii) and the step of drying the film.

115. The method of any one of claims 110 to 114, further comprising installing an electrode in contact with the film.

116. The method of claim 115, further comprising the step of thermally annealing the film subsequent to installing the electrode.

117. The method of any one of claims 105 to 116, wherein the substrate comprises a conductor layer.

118. The method of claim 117, wherein the solution is applied directly to the conductor layer.

119. The method of any one of claims 105 to 118, wherein the solution further comprises an electron acceptor.

120. The method of claim 119, wherein the electron acceptor is selected from the group consisting of a fullerene, a fullerene derivative, a nanoparticle, nanocrystal, quantum dot, or any combination thereof.

121. The method of claim 120, wherein the quantum dot comprises CdSe, CdTe, CdS, PbS, PbSe, CuInS₂, CuInSe₂, Cd₃As₂, Cd₃P₂, or any combination of any of the foregoing.

122. The method of any one of claims 119 to 121, wherein the photovoltaic device is a solar cell having a power conversion efficiency of at least 2.7% when exposed to simulated sunlight of an intensity of 1 Sun under AM1.5 G conditions.

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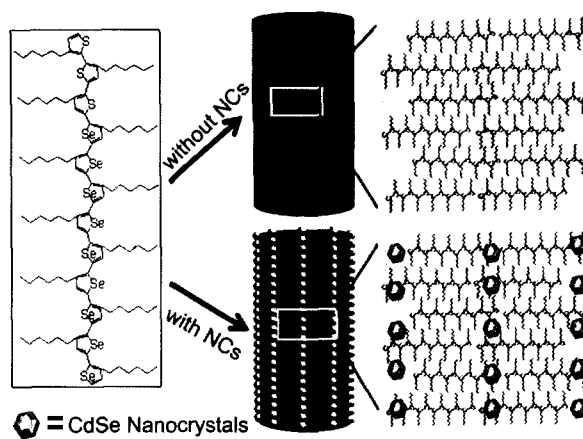


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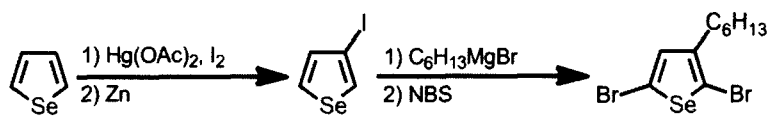


Figure 2

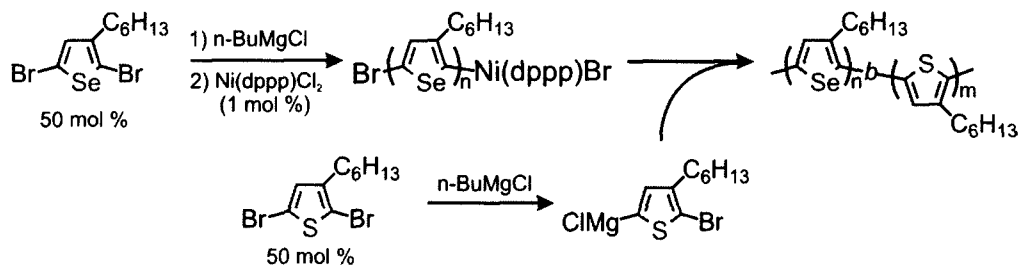
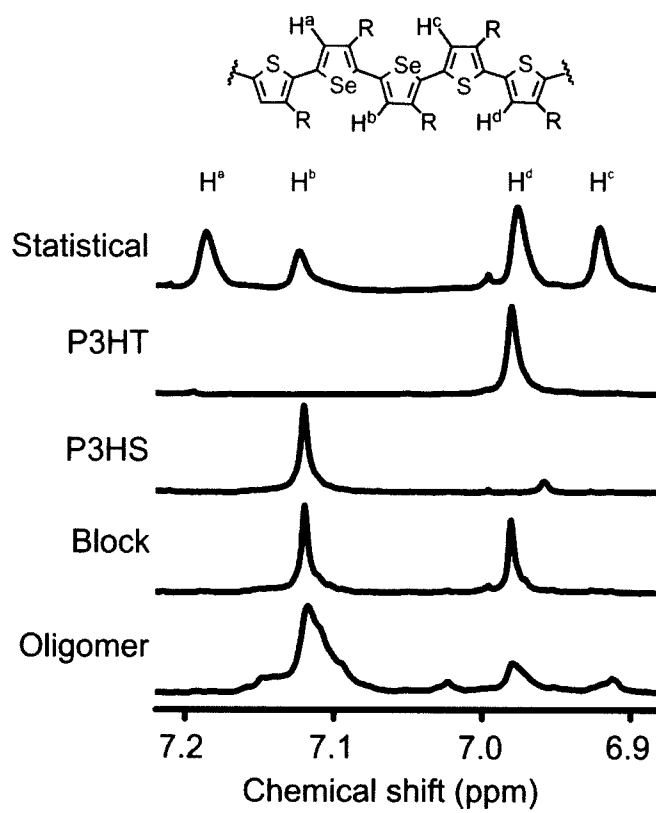


Figure 3

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**Figure 4**

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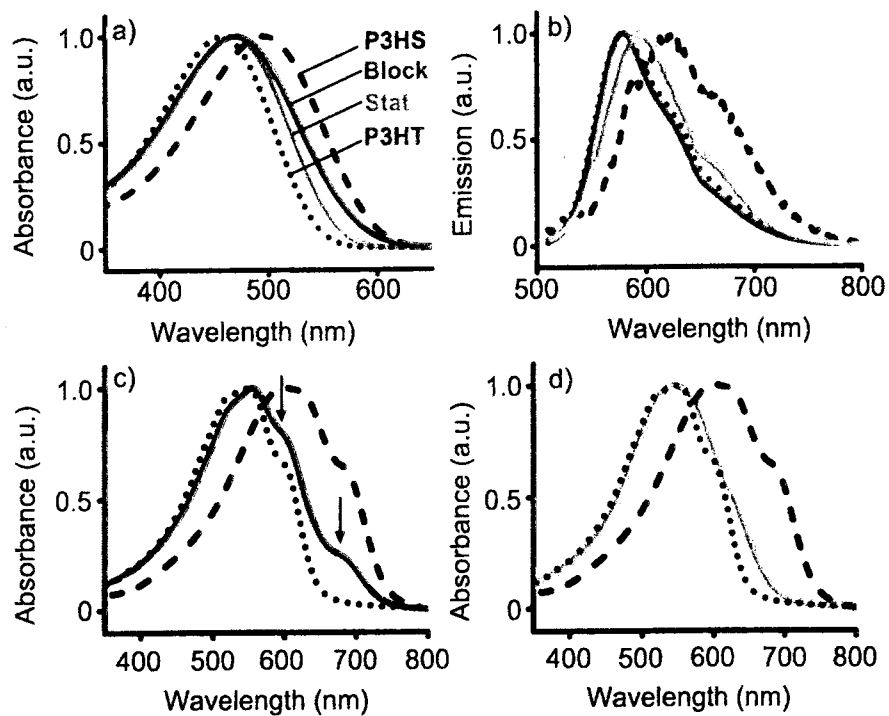


Figure 5

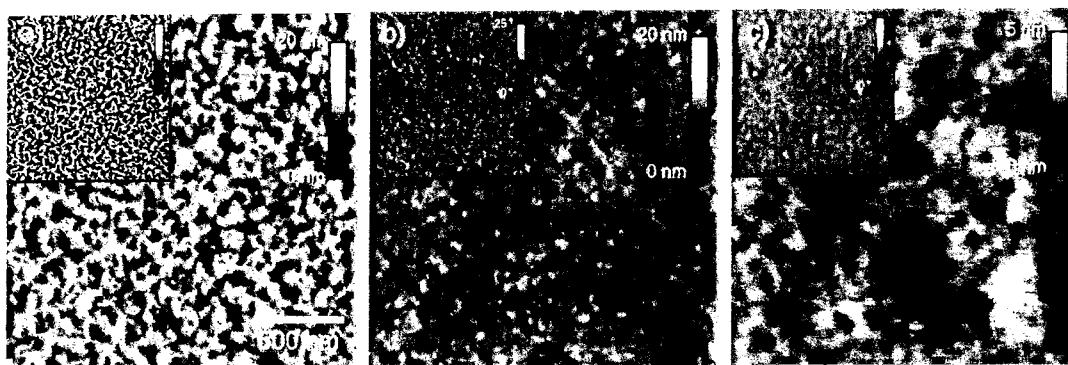
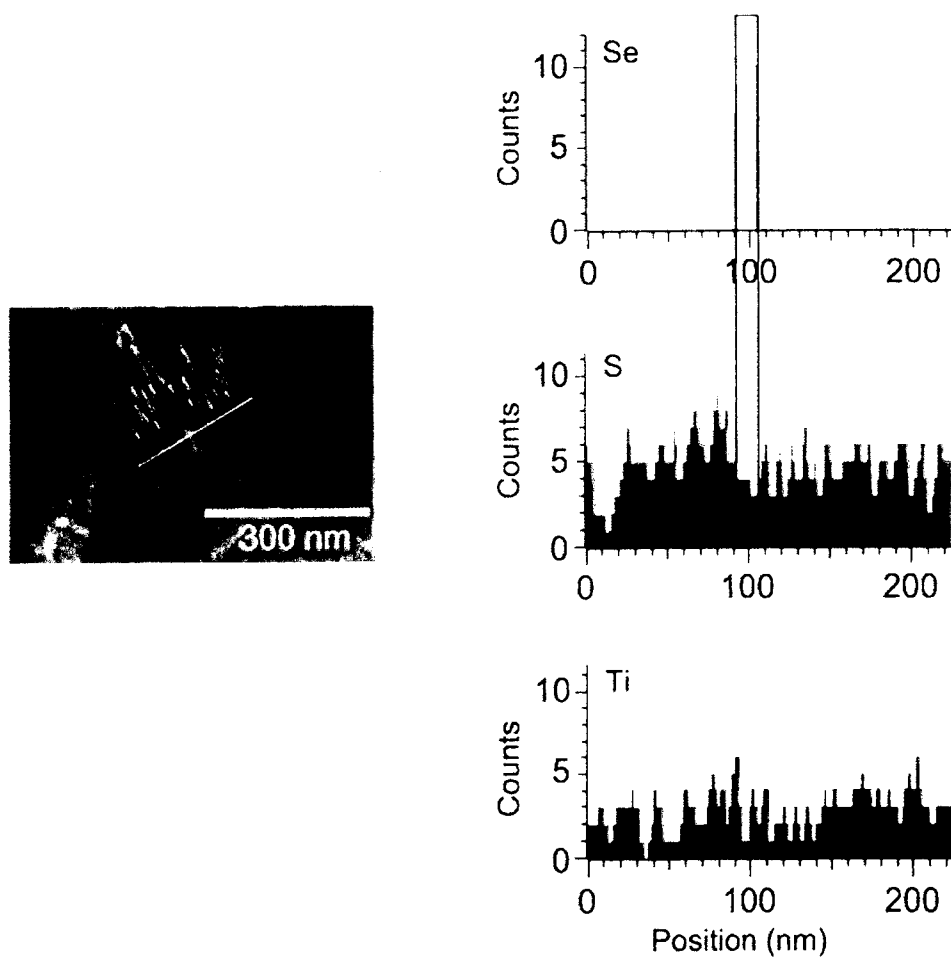
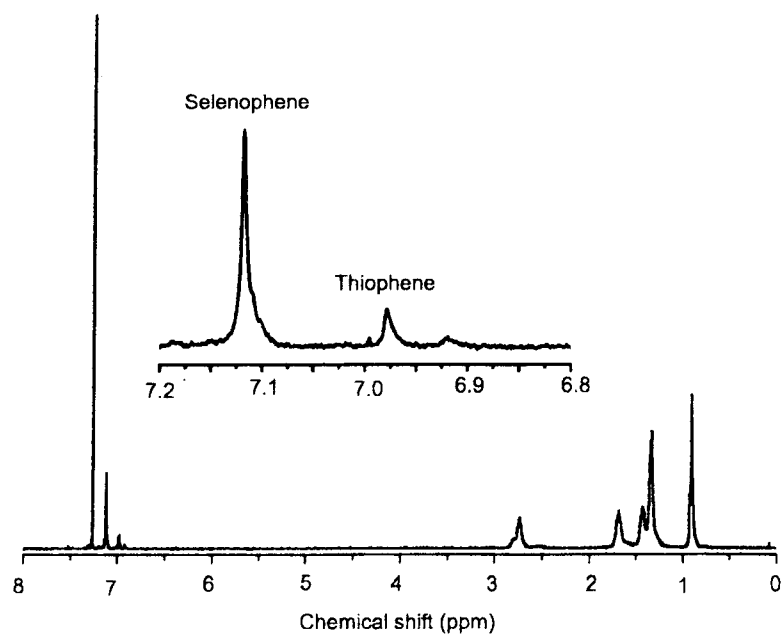


Figure 6

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**Figure 7****Figure 8**

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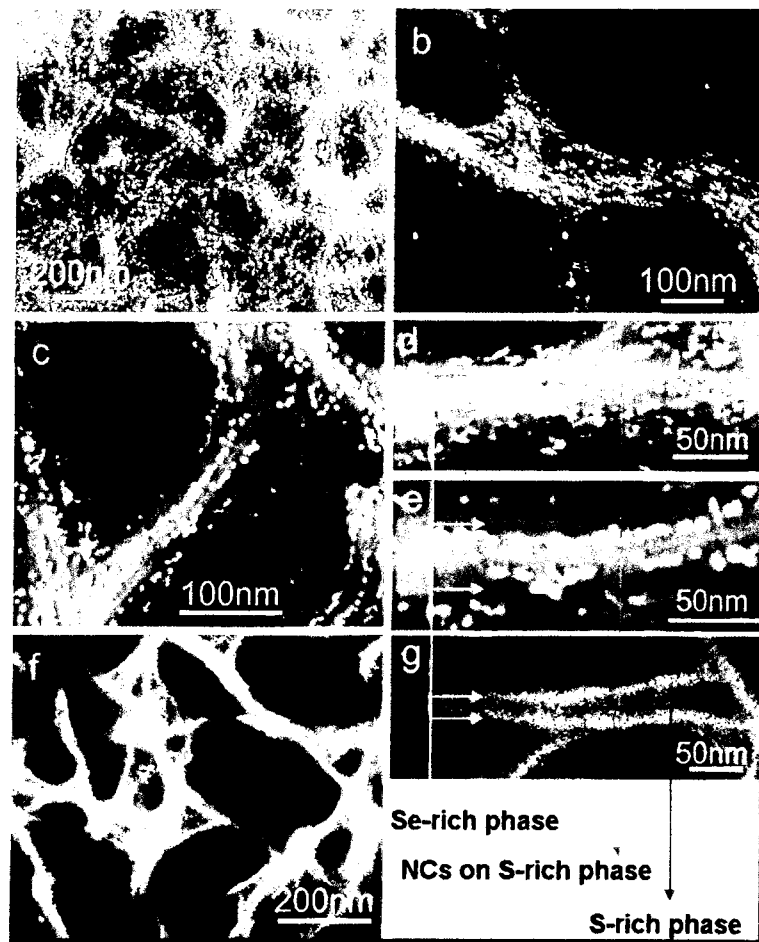
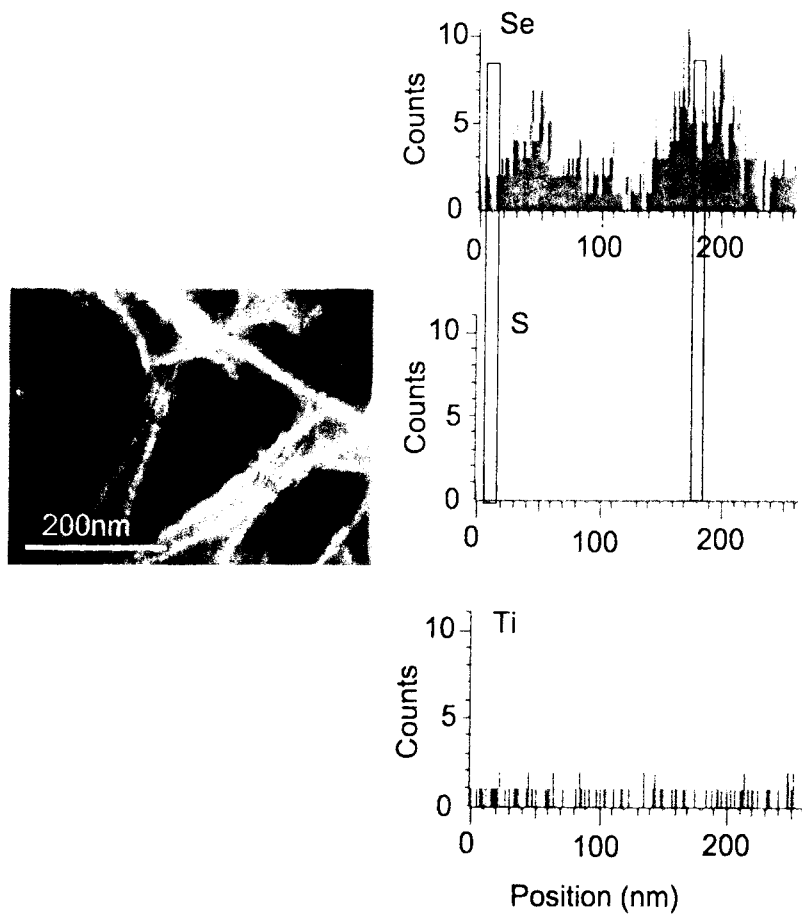


Figure 9

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**Figure 10**

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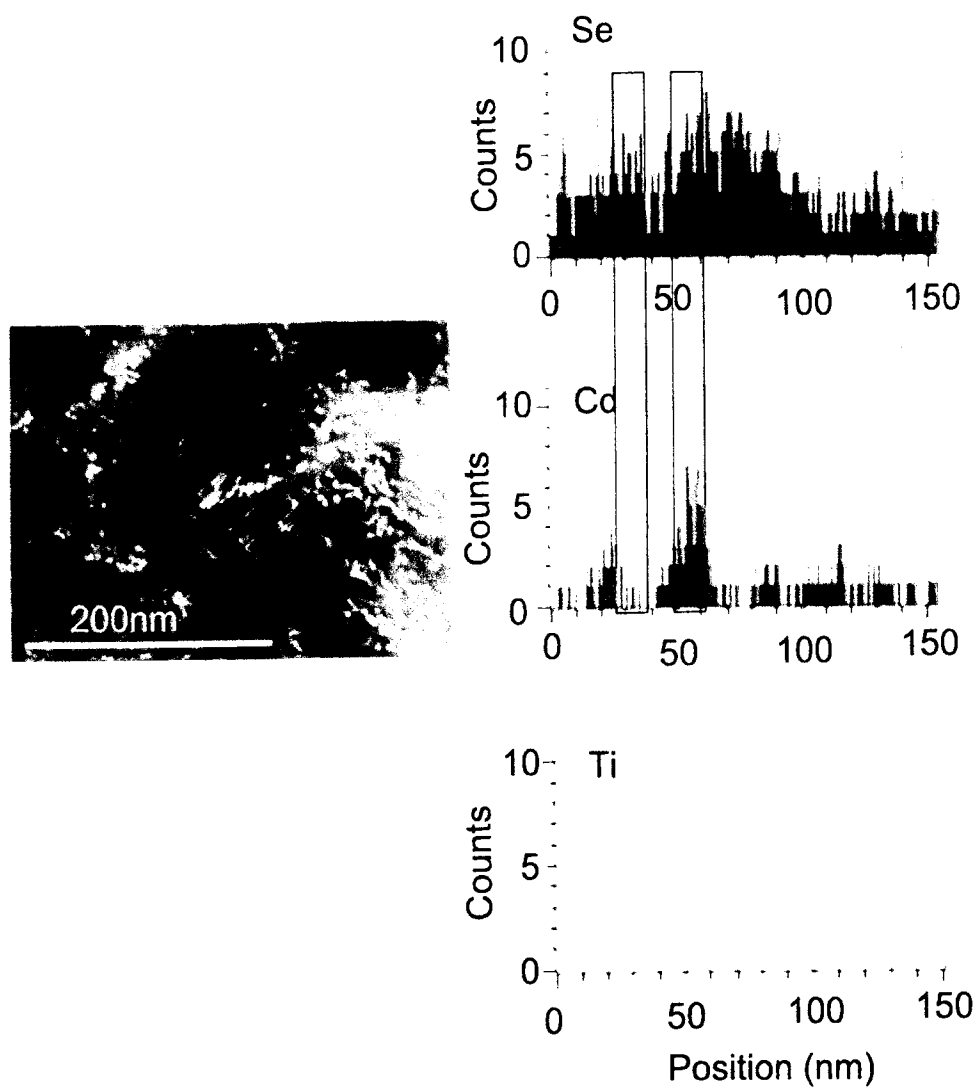


Figure 11

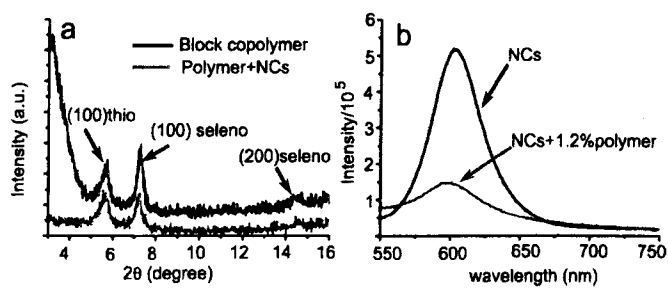


Figure 12

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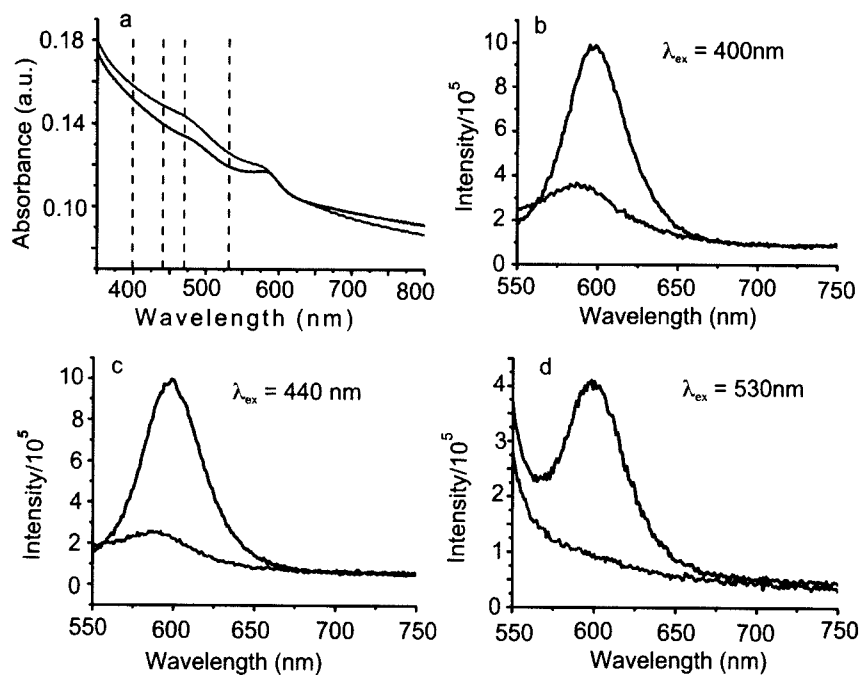


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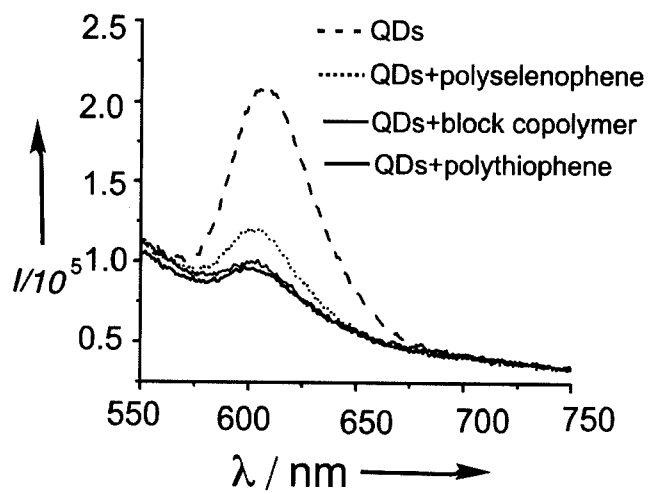


Figure 14

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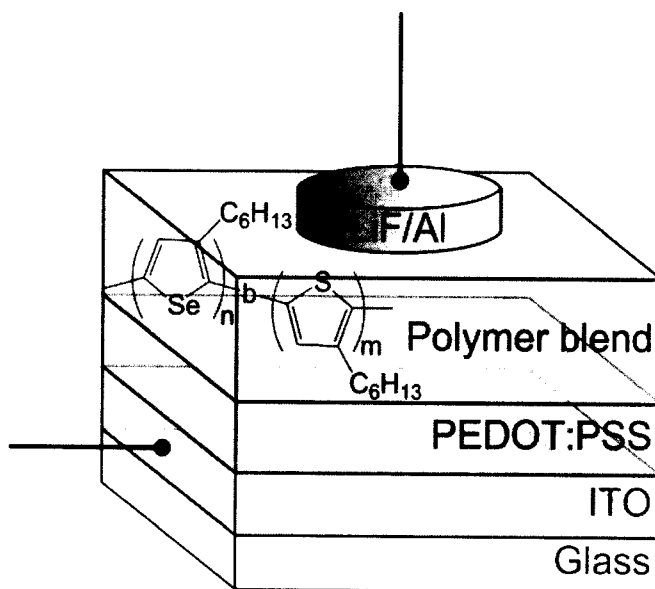


Figure 15

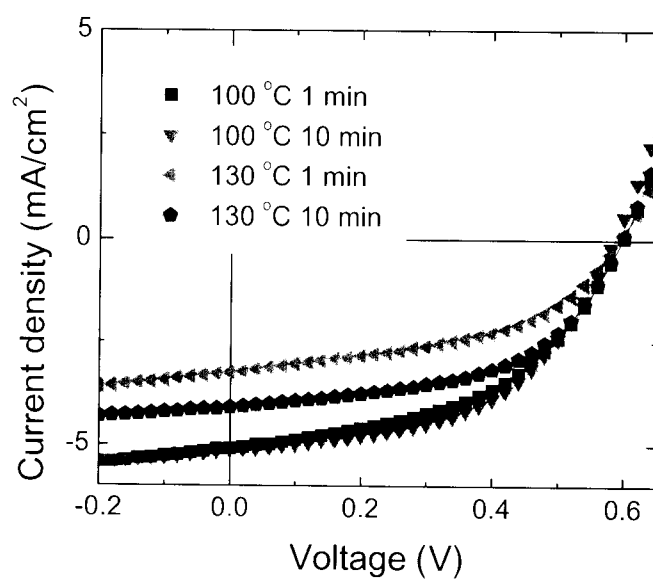


Figure 16

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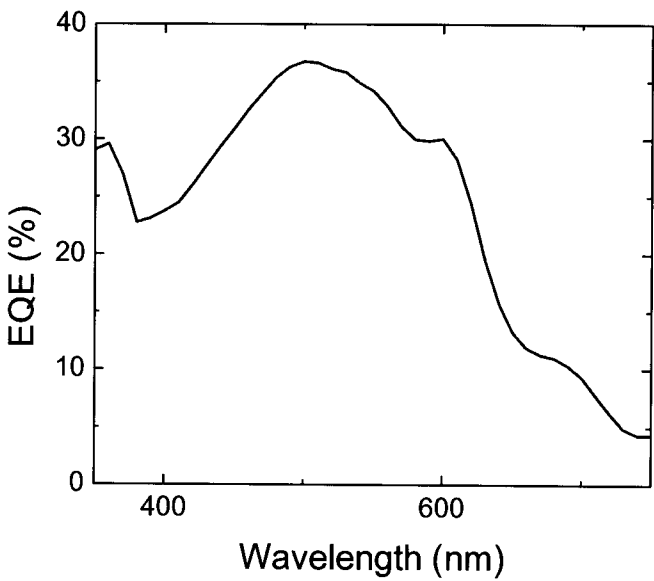


Figure 17

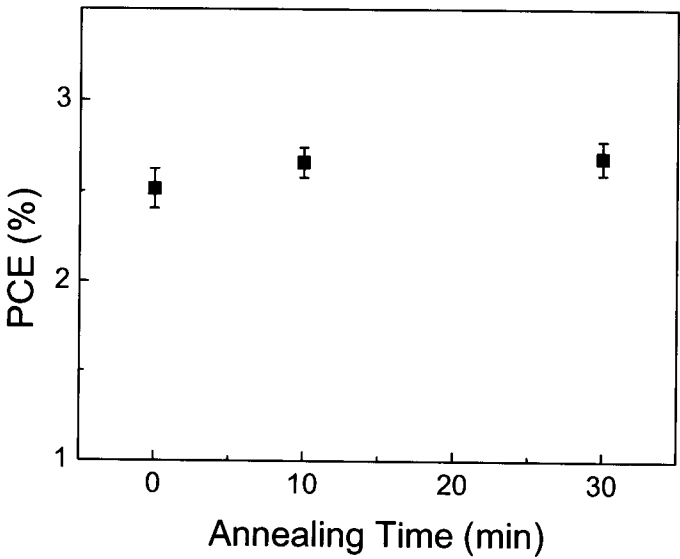


Figure 18

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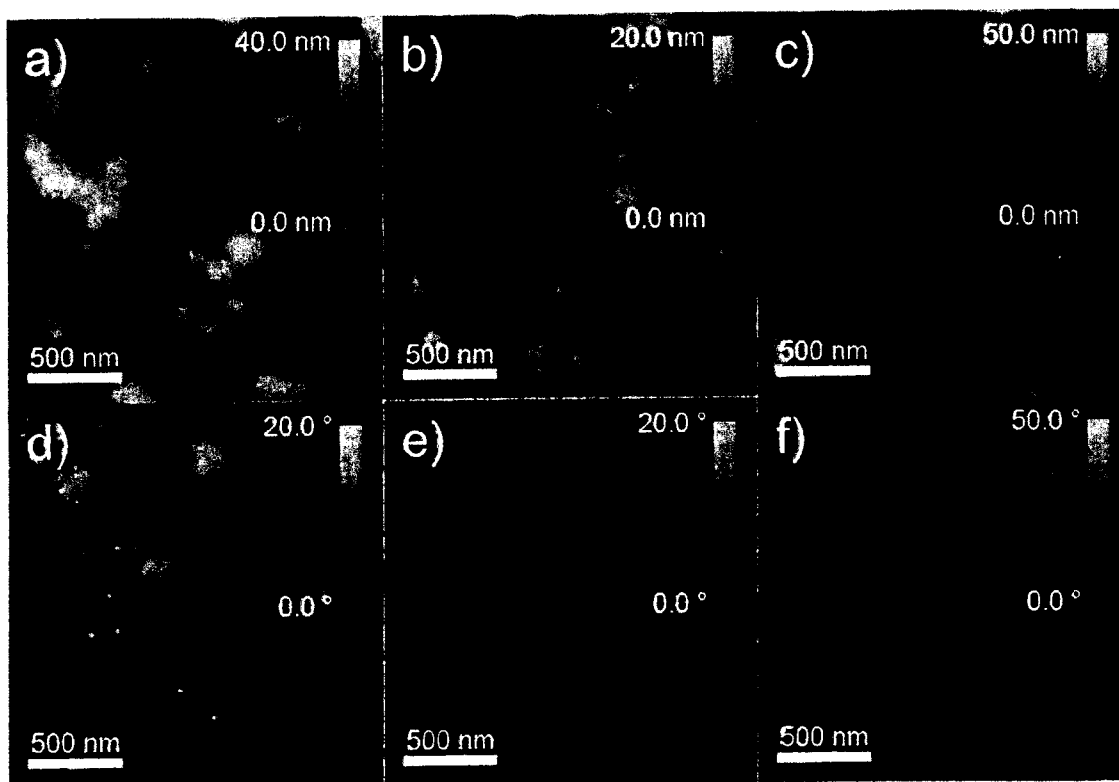


Figure 19

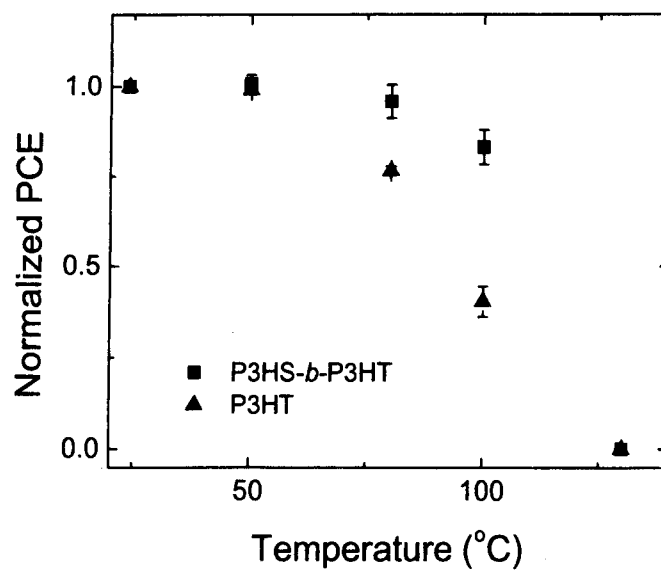
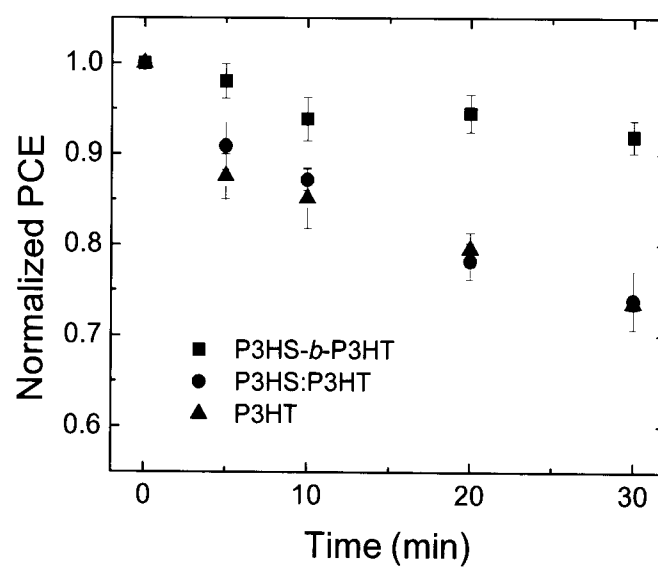
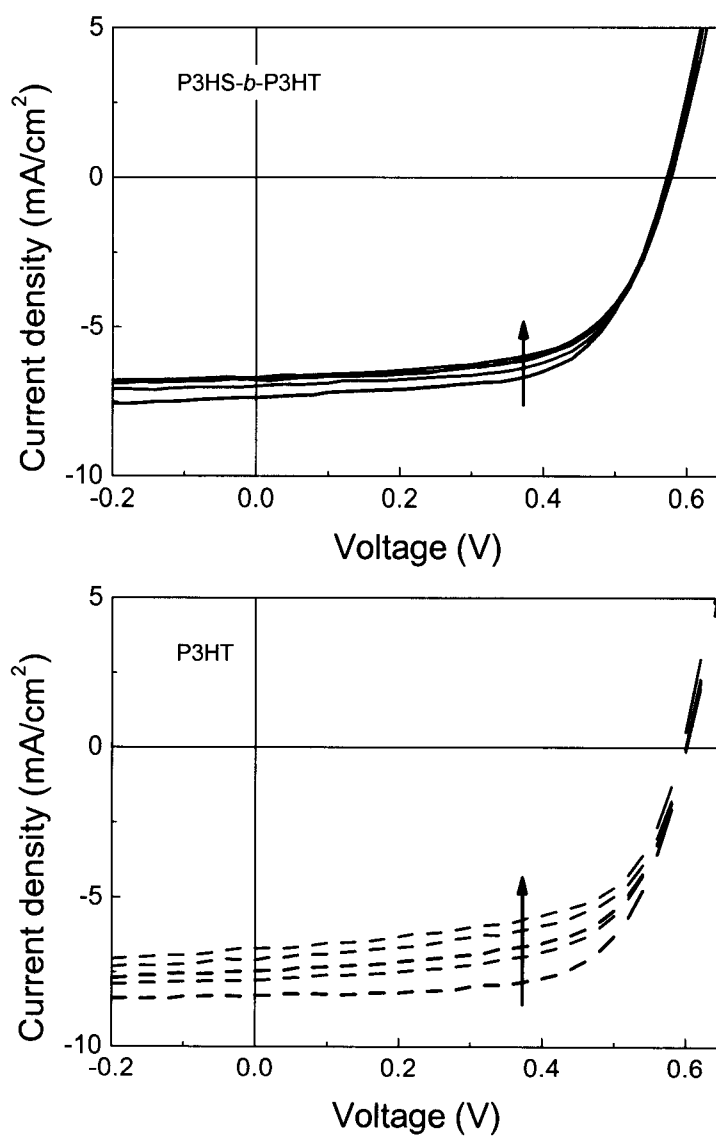


Figure 20

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**Figure 21**

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**Figure 22**

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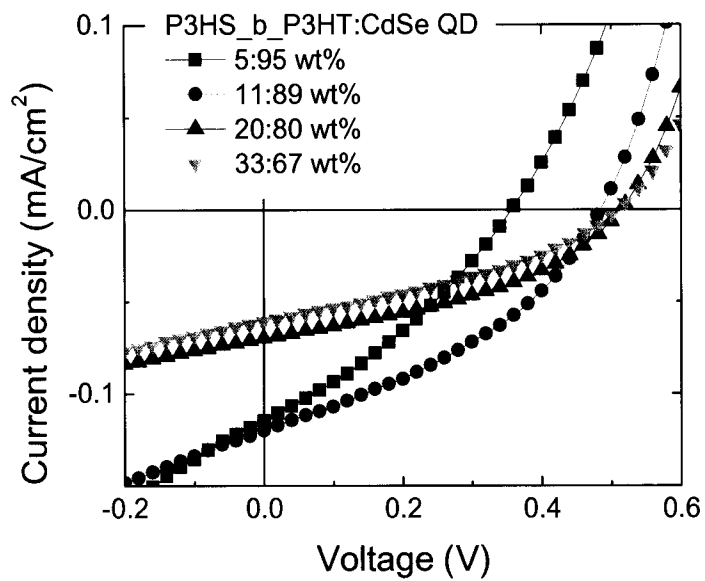


Figure 23

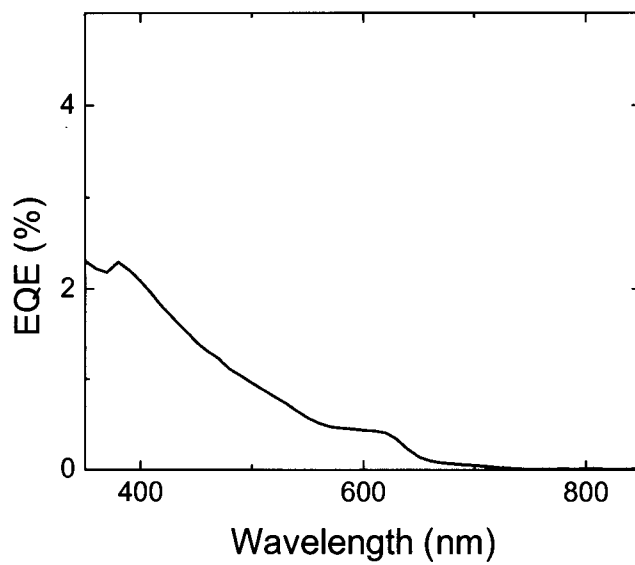


Figure 24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/000498

A. CLASSIFICATION OF SUBJECT MATTER IPC: C08G 81/00 (2006.01) , C08G 61/12 (2006.01) , C08K 3/00 (2006.01) , C08K 5/00 (2006.01) , C08L 65/00 (2006.01) , C30B 29/58 (2006.01) (more IPCs on the last page) 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) C08G 81/00, C08G 61/12, C08K 3/00, C08K 5/00, C08L 65/00, C30B 29/58, H01L 51/30, H01L Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched N/A Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Databases: STN; Canadian Patent Database (Intellect); Total Patent; Royal Society of Chemistry publication search; ScienceDirect; Scopus; Google Scholar; Espacenet; American Chemical Society publication search key words: selenophene-thiophene copolymers; polymers and electronics; all-conjugated diblock copolymers; block copolymer and semiconductor composite materials; thiophene and selenophene and optoelectronic and polymer; block copolymer and optoelectronic; poly(3-hexylthiophene); applicant search																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>D1: "Controlling Phase Separation and Optical Properties in Conjugated Polymers through Selenophene-Thiophene copolymerization". whole document Hollinger, J et al. <i>J. Am. Chem. Soc.</i> 2010, 132, 8546-8547</td> <td>1-122</td> </tr> <tr> <td>X</td> <td>D2: "Block Copolymer Containing Poly(3-hexylthiophene) and Poly(4-vinylpyridine): Synthesis and its Interaction with CdSe Quantum Dots for Hybrid Organic Applications". whole document Palaniappan, K et al. <i>Journal of Polymer Science Part A: Polymer Chemistry</i> 2011, 49, 1802-1808</td> <td>1, 4, 7, 10, 16-43, 46, 54-122</td> </tr> <tr> <td>X</td> <td>D3: "A First Approach to White Organic Electroluminescence Device from a Single Rod-Coil Poly[thiophene-block-(N-vinylcarbazole)] Diblock Copolymer". whole document Heo, M et al. <i>Macromol. Rapid Commun.</i> 2010, 31, 2047-2052</td> <td>1, 4, 7, 10, 16-43, 46, 54-122</td> </tr> <tr> <td>X</td> <td>D4: "Polythiophene-block-polyfluorene and Polythiophene-block-poly(fluorene-co-benzothiazole): Insights into the Self-Assembly of All-Conjugated Block Copolymers". whole document Verduzco, R et al.</td> <td>1, 4, 7, 10, 16-43, 46, 54-122</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	D1: "Controlling Phase Separation and Optical Properties in Conjugated Polymers through Selenophene-Thiophene copolymerization". whole document Hollinger, J et al. <i>J. Am. Chem. Soc.</i> 2010 , 132, 8546-8547	1-122	X	D2: "Block Copolymer Containing Poly(3-hexylthiophene) and Poly(4-vinylpyridine): Synthesis and its Interaction with CdSe Quantum Dots for Hybrid Organic Applications". whole document Palaniappan, K et al. <i>Journal of Polymer Science Part A: Polymer Chemistry</i> 2011 , 49, 1802-1808	1, 4, 7, 10, 16-43, 46, 54-122	X	D3: "A First Approach to White Organic Electroluminescence Device from a Single Rod-Coil Poly[thiophene-block-(N-vinylcarbazole)] Diblock Copolymer". whole document Heo, M et al. <i>Macromol. Rapid Commun.</i> 2010 , 31, 2047-2052	1, 4, 7, 10, 16-43, 46, 54-122	X	D4: "Polythiophene-block-polyfluorene and Polythiophene-block-poly(fluorene-co-benzothiazole): Insights into the Self-Assembly of All-Conjugated Block Copolymers". whole document Verduzco, R et al.	1, 4, 7, 10, 16-43, 46, 54-122
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X	D3: "A First Approach to White Organic Electroluminescence Device from a Single Rod-Coil Poly[thiophene-block-(N-vinylcarbazole)] Diblock Copolymer". whole document Heo, M et al. <i>Macromol. Rapid Commun.</i> 2010 , 31, 2047-2052	1, 4, 7, 10, 16-43, 46, 54-122															
X	D4: "Polythiophene-block-polyfluorene and Polythiophene-block-poly(fluorene-co-benzothiazole): Insights into the Self-Assembly of All-Conjugated Block Copolymers". whole document Verduzco, R et al.	1, 4, 7, 10, 16-43, 46, 54-122															
[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.																	
<table border="1"> <tbody> <tr> <td>* Special categories of cited documents :</td> <td>"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</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </tbody> </table>			* Special categories of cited documents :	"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	"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent but published on or after the international filing date	"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	"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)	"&" document member of the same patent family	"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				
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Date of the actual completion of the international search 27 August 2012 (27-08-2012)		Date of mailing of the international search report 14 September 2012 (14-09-2012)															
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 Wendy Young (819) 934-0477															

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/000498

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