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Functional semiconductors targeting copolymer architectures and hybrid nanostructures

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Abstract

The introduction of functional units onto semiconducting polymers either as side chains or at the α- and ω-ends of polymeric chains is the method of choice in order to impose additional functions to the final semiconducting materials when aiming specific applications. Moreover, the functionalization approach provides a route to further complex macromolecular architectures as well as the generation of hybrid materials through the covalent attachment of the semiconductor to carbon nanostructures or to inorganic nanoparticles. Via this prospective an outline over functionalized and hybrid semiconducting polymers is provided along with possible paths of future research toward functional and hybrid semiconductors.

Introduction

The unique properties of organic conducting polymers were first discovered by Heeger, Shirakawa, and MacDiarmid back in the 1970s. This discovery was the genesis of an enormous amount of work in the area of organic electronics and was finally honored with the Nobel Prize in Chemistry in 2000.[1] Conjugated semiconducting polymers offer broad applications in the field of molecular electronics. Perhaps the most attractive research area in polymers nowadays is the development of novel semiconducting polymers for organic photovoltaics (OPVs), organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), sensors, etc.[2] Their properties modulation via precise control of the molecular structure has populated a vast number of publications, patents, and further technological breakthroughs in the past 2–3 decades. Conjugated polymers and oligomers offer the unique capability of tuning the final semiconducting materials' properties via a correct choice of the chemical structure and the synthetic methodology, the variation of conjugation length, and the substitution pattern of side groups. Besides their inherent function of charge carrier generation and transport and their nanomorphology based on π–π-stacking interactions, the alteration of their exact chemical structure, and the introduction of side or main chain functionalities, meaning moieties that can lead to further reactions and/or interactions, greatly expand their properties and potentiality.

Net, unsubstituted conjugated polymers such as poly (p-phenylene), poly(p-phenylene vinylene), etc., suffer from low to negligible solubilities due to extended π-stacking prohibiting thus, their processing from solution to thin films. In the vast number of cases, the semiconducting macromolecular chains are decorated with alkyl, alkoxyl, branched, or even dendritic side units which serve a dual scope: to impose solubility and processability to the final semiconductor as well as to enhance nanophase ordering and crystallization in the thin film which are essential for charge transport in most of the organic electronic devices.

On the other hand, and since their discovery back in the early 1990s, fullerenes and carbon nanotubes (CNTs) have attracted scientific interest as promising materials for novel applications. The realization of their electronic properties opened new possibilities for technological applications such as in organic electronics. Almost 20 years after the realization of the bulk heterojunction photovoltaics (BHJ PVs), based on the combination of polymeric conjugated electron donors and fullerene derivatives as electron acceptors, the efficiency of these systems has exceeded 10% boosting their perspective for commercialization. Certain figures of BHJ PVs such as reduced cost, mechanical flexibility, impact resistance, optical transparency, large area coverage, and printability are their most prominent advantages over the competing silicon-based PV technologies. The active layer of a typical organic PV cell is composed of a polymeric semiconductor, as the electron donor, blended with a fullerene derivative, as the electron acceptor. The known semiconducting conjugated polymers poly (1,4-phenylene-vinylene)s (PPVs) and poly(3-hexylthiophene) (P3HT) were initially used as the electron donors, that after light absorption generate excitons which dissociate to provide electrons to a neighboring electron-accepting phase. Efficient matching of the energy levels of the electron donor and the

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electron acceptor, the maximum light absorption and the required morphology of a stable, nanophase-separated system with bicontinuous structures are the crucial parameters that determine the final PV efficiency. Open questions in the OPVs technology still are the design and scaling up of more efficient electron donors, the development of appropriate organic electron acceptors, and the correct matching of the favorable electron donor and electron acceptor into the desired nanoscaled morphology of a bicontinuous interpenetrating network.

The synthesis of new materials aiming to improve the energy efficiency of PV devices is a primary research area of focus of the scientific community. Attempts to this direction are either to find even better polymeric electron donors, or perhaps more efficient electron acceptors, or to improve the performance of the overall system with methodologies that will drastically contribute to the optimization of device's performance, reaching values higher than 10%.[3,4]

Besides recent enhancements in device performance mainly due to the development of a large number of more effective polymeric electron donors there is still space and demand for efficiency improvement. This can be achieved through the control and stabilization of the active layers morphology through the use of copolymers with electron donor and electron acceptor units and hybrid materials modified with carbon nanostructures. These new hybrid materials are expected to have improved properties, controlled energy levels and to contribute to the better mixing of the photoactive electron donor and acceptor materials improving thus, the morphology and hence the efficiency of the PV device.

The electron donor in a PV device is the responsible material for the absorption of solar light. The maximum of the electromagnetic radiation of the visible spectrum is near IR and thus the maximum of the electron donors' absorption should be located in that region. However, most polymers absorb only a small part of the incoming light. Based on the emission spectrum of the sun, it is calculated that the band gap of the optimal polymeric donor should be approximately 1.5 eV. Essential characteristics of the electron donor are also good hole mobility and the capacity to create in combination with the electron acceptor a stable film on the device which will lead to the appropriate morphology.

Herein, we will emphasize on semiconducting polymers being substituted by functional groups (e.g., hydroxyl, carboxylic acid or ester, halogen, azide, etc.) aiming thereafter to further modify, copolymerize or create hybrids with carbon nanostructures.

Functional semiconducting polymers

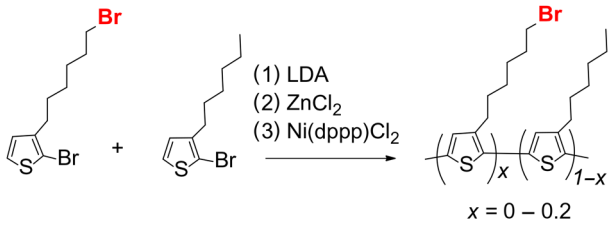
Organic semiconductors have attracted much attention, due to their versatility, promise for larger scale, lower cost, and easier production of electronic devices as compared with their inorganic counterparts. A potential advantage of utilizing conjugated polymers in such applications is the ability to tune the properties of the polymer at the molecular level. Tuning is typically accomplished through synthetic modification, which permits the incorporation of additional functionalities. The ability to modify these properties is of the utmost importance for the efficient application of these materials. Soluble, stable systems are required for their processing, and the desirable properties of these polymers are dependent on the extent of conjugation. Increased conjugation lowers the band gap and results in an enhancement of the thermal population of the conduction band, thus increasing the number of intrinsic charge carriers.

The most widely employed methods for the synthesis of the conjugated polymers for optoelectronic devices are (cross-) coupling reactions mediating Pd or Ni catalysts. As such Suzuki, Stille, Heck, Kumada coupling and more recently direct-arylation reactions are commonly employed and can tolerate various heteroatoms and substitution patterns of the involved monomers.

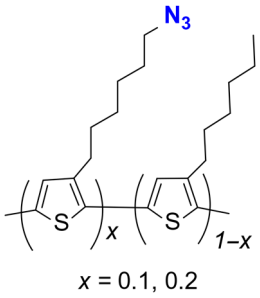
The need for heteoatoms incorporated in polymer semiconductors was early recognized since they can alter and effectively change the band gap of the polymer increasing the absorption wavelengths as needed in solar cell electron donors or lowering the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) levels resulting in p- or n- semiconductors. Nitrogen and oxygen atoms are electron withdrawing leading to better electron transporting properties. Poly(benzimidazobenzophenanthroline) is an excellent example of a potential electron acceptor containing nitrogen heterocycle or otherwise an n-type conjugated ladder polymer that has an ionization energy (HOMO level) of 5.9 eV, an electron affinity (LUMO level) of 4.0 eV, excellent thermal stability in air and exceptionally high field-effect electron mobility.[5–7]

As part of the heteroatom containing semiconducting polymers family, the polythiophenes case are probably the most studied materials as polymeric electron donors, considered the benchmark polymers in most organic electronic applications. Every respectable novel material developed and tested "must" be compared and prove itself versus P3HT. This is nowadays the reference polymer electron donor especially when it comes to polymer solar cells. In general, polythiophenes are stable materials applicable in almost all environmentally friendly energy-producing devices and machines.[8,9] In particular, poly(3-substituted thiophene)s are one of the most studied polymer groups for (semi)conductor/optical applications, thanks to the well-understood synthetic methods for high molecular weight and regioregular polymers and their good solubility and processability.[10] Of course, the grignard metathesis (GRIM)[11] or Ni-catalyzed chain-growth polymerization[12] or Kumada catalyst-transfer polycondensation[13–15] has been widely employed since it can produce P3ATs of high regioregularity and molecular weight that moreover carry "living" bromine chain ends[16] which can be further modified either in situ or ex situ the polymerization reaction. Moreover, regioregular head-to-tail rr-P3HT can be electrophilically substituted at the four-position of the thiophene ring. Introduction of side bromine groups is especially useful for further reaction through typical Suzuki, Stille, and Heck coupling conditions leading to poly(thiophene)s possessing aryl, vinyl, alkynyl, etc. side-chain groups.[17,18]

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Scheme 1. P3HT-Br copolymers prepared by the McCullough method.[16]



Scheme 2. Azide side-functionalized rr-P3HT copolymers.[27]

In several cases, the preparation of a multi-macroinitiator P3HT which possesses the desired light absorption and electron-donating function was demonstrated and thereafter the development of a second segment via polymerization of the proper vinylic monomer was performed. The post-functionalized P3ATs retain their optical properties if the functionalization degree remains low (typically up to 10%).[19–24]

As will be explained in the below section of hybrid semiconducting polymer–fullerene systems, several P3HT copolymers have been used to develop hybrids acting as compatibilizers of the active P3HT:PCBM layer. Additionally the crosslinking concept could lead to the stabilization of the active layer's morphology.[25] Below a few representative examples of crosslinking the electron donors in OPVs and OTFTs are given, which also apply to the case of side group functionalities inserted into P3HT.

Bromine-functionalized regioregular poly(3-hexylthiophene) (P3HT-Br) copolymers (Scheme 1) were prepared by copolymerization of 2-bromo-3-(6-bromohexyl) thiophene and 2-bromo-3-hexylthiophene by the McCullough method.[16] The P3HT-Br copolymers were cross-linked, via a radical mechanism initiated by the photochemical cleavage of the C–Br bonds under ultraviolet (UV) irradiation at 254 nm and were used as electron donors in both BHJ and bilayer-type PV devices that proved to be thermally more stable when compared with devices based on non-crosslinked plain P3HT.[26]

Using once again the above-described side bromine bearing copolymers Kim et al. replaced the bromine with azide units at the end of the alkyl chains of P3HT. The P3HT–azide copolymers (Scheme 2) were used in OTFT devices after crosslinking upon exposure to UV light. Moreover, the P3HT–azide polymers formed fullerene-attached diblock copolymers. Therefore the P3HT–azide copolymers were employed as in situ compatibilizers in P3HT/PCBM BHJs, affording efficient and also thermally stable OPVs with suppressed macrophase separation as seen in Fig. 1.[27]

Anthracene end-capped P3HT has also been prepared and studied in respect to the stabilization of its blend with PCBM after UV treatment of the blends that promotes a [2 + 2] cycloaddition of the anthracene moieties with the fullerene species.[28]

As already mentioned the "living" bromine end chain groups of P3AT can be in situ or ex situ transformed to functional moieties affording end functionalized P3ATs.[29]

A vast number of P3HT-containing block copolymers have been reported employing end functionalized macromolecules where the end functionality can initiate the polymerization of different monomers or can react with α, ω, or α-functionalized polymeric chains.[30] For example, Urien et al. synthesized a series of P3HT-containing di- and triblock copolymers from alkyne end-functionalized P3HT and azide end-functionalized polystyrenes.[31] Segalman and co-workers reported block copolymers prepared from an ethynyl-terminated P3HT that was reacted under "click" chemistry conditions with a polyacrylate polymerized from an azido-functionalized initiator and that

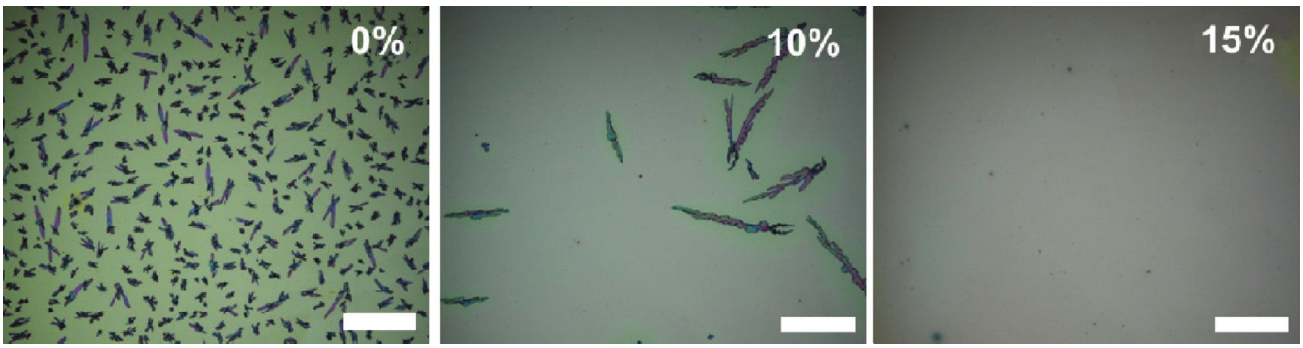
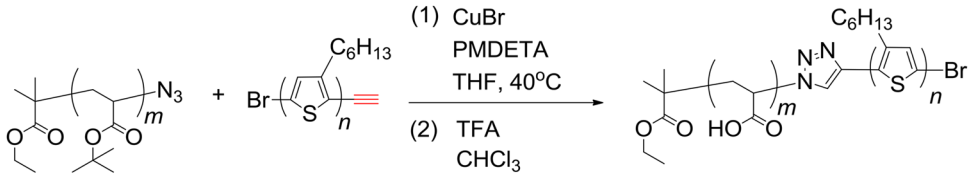


Figure 1. Optical microscopy images of the P3HT/PCBM films containing 0%, 10%, or 15% P3HT-azide10 copolymer after annealing at 150 °C for 24 h. Scale bar =100 μm. Adapted with permission from Ref. 27, copyright (2012) American Chemical Society.

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Scheme 3. Synthesis of P3HT-b-PAA.[35]

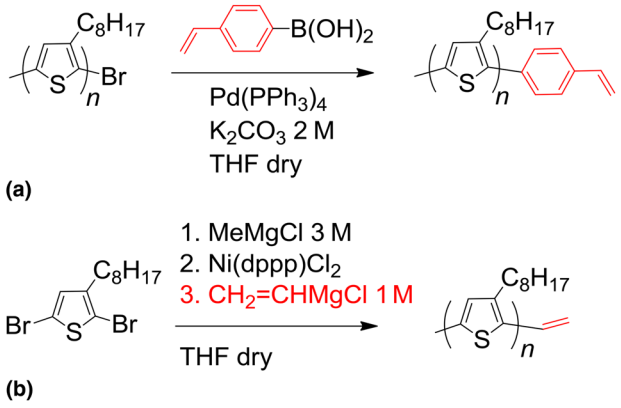
moreover carried side electron accepting perylene bisimide moieties.[32] McCullough and co-workers reported a P3HT-block-poly(acrylic acid) (P3HT-b-PAA) copolymer that showed a solvatochromic behavior in a variety of polar and non-polar solvents.[33] Hadziioannou and co-workers reported on the post-functionalization of P3HT affording ω-thiol-, ω-carboxylic acid, ω-acrylate-, and ω-methacrylate-terminated P3HT from which graft copolymers with polyisoprene, poly(vinyl alcohol), or poly(butyl acrylate) coils were synthesized following the "grafting onto" or the "grafting through" methods.[34] In addition, Bielawski and co-workers reported an in situ synthesis of ethynyl end functionalized P3HT of high purity that facilitated access to P3HT-b-PAA which self-assembled into hierarchical structures (Scheme 3).[35]

Ethynyl end-functionalized P3HT has been most recently used for the preparation of P3HT-block-poly-(neopentyl p-styrenesulfonate) copolymes via its click chemistry with azide end-functional protected polystyrene sulfonate blocks.[36]

Combination of click chemistry and nitroxide-mediated radical polymerization (NMRP) was used by Lohwasser et al. for the incorporation of P3HTs segments into amphiphilic block copolymers at which the alkyne-terminated P3HT performed a copper-catalyzed azide–alkyne click reaction, forming a macroinitiator for NMRP that polymerized 4-vinylpyridine (4VP) (Scheme 4)[37]

Allyl end-functional P3HT was also modified to hydroxyl end-functional P3HT that performed Steglich esterification with poly(ethylene oxide) (PEO) chains bearing end carboxylic acid units, leading to P3HT-block-PEO copolymers.[38]

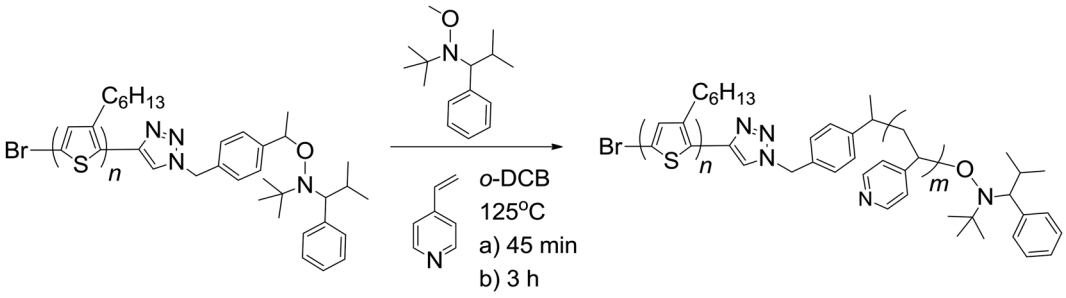
Macromonomer ω-end vinyl P3ATs can be prepared either via a Suzuki coupling of the bromine end-group with styryl-



Scheme 5. Synthesis of ω-end vinyl P3ATs (a) with a post-polymerization Suzuki coupling reaction, (b) via in situ introduction of the double bonds at the end of the GRIM polymerization.[39]

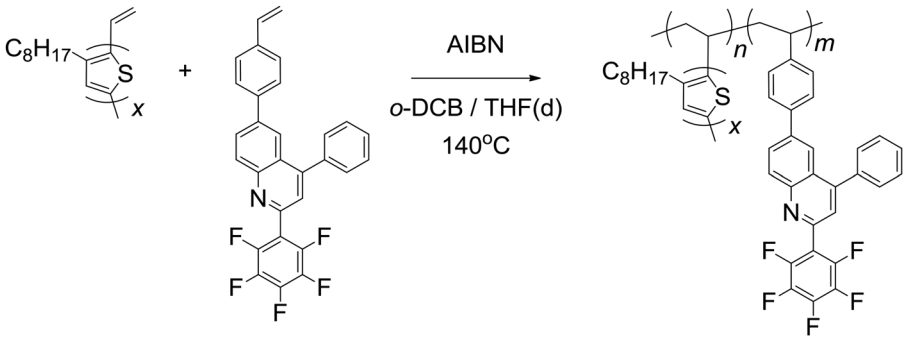
boronic acid or directly in the polymerization medium by adding a vinyl magnesium halide as soon as the polymerization has come to its end (Scheme 5).

Such 2-vinyl terminated regioregular poly(3-octylthiophene)[39] can be used thereafter as macromonomers in copolymerization with other semiconducting or not comonomers. An example of copolymers containing vinyl-P3HT blocks that are prepared via free radical polymerization (FRP) are given in Scheme 6, in which a potential electron-accepting comonomer, vinylphenyl perfluorophenyl-phenylquinoline has been employed.[40] The perfluorophenyl group was specifically selected in this case as an electron withdrawing group with the potential to lower even more the LUMO level of the quinoline electron acceptor.



Scheme 4. Incorporation of P3HT in combined NMRP with click chemistry.[37]

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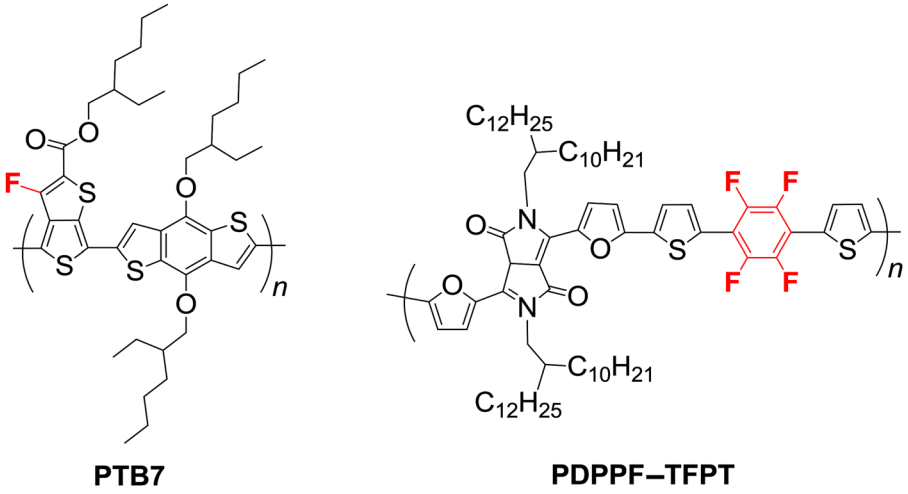
Scheme 6. Preparation of P3HT random copolymers via FRP.[40]

However, and most importantly, these perfluorophenylquinoline containing copolymers were used for the development of hybrid materials comprising fullerene species as will be described in more detail in the below hybrids' section.

Fluorine-substituted oligomeric or polymeric semiconductors have been developed in many cases trying to make use of the electron-withdrawing fluorinated aromatic rings.[41,42] Highly fluorinated systems such as perfluoroarenethiophenes, exhibit unique molecular-packing and charge-transport characteristics in comparison with the corresponding fluorine-free analogs[43] Incorporating the fluorinated units serves to lower both the LUMO and HOMO energies of the materials and also facilitates planarization. Lowering of the HOMO energy level to below −4.9 eV, the level at which electrochemical reactions with wet oxygen can occur, is desirable for improving the ambient stability of polythiophenes.[44]

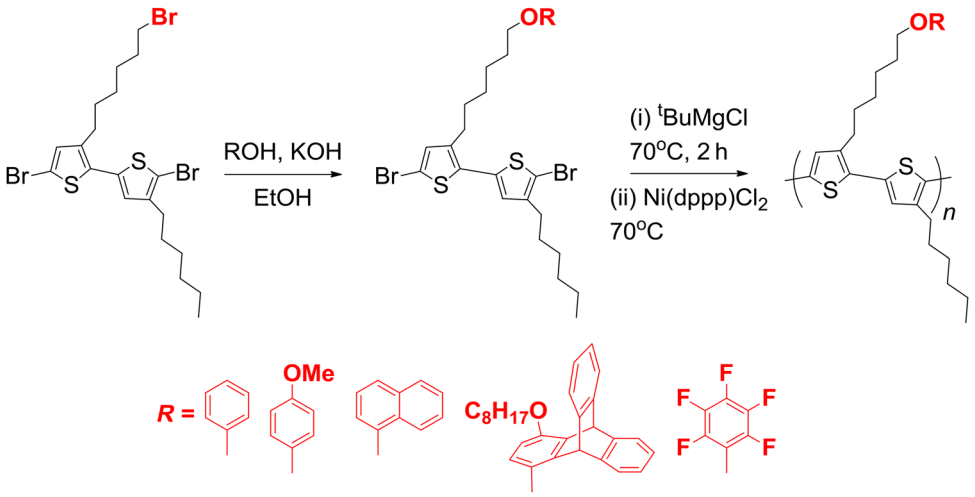
The case of the PTB7 electron donor (Scheme 7) is a characteristic study in which the presence of the fluorine atom leads to a lower HOMO level, thus enhancing the V_{oc} parameter. This polymer exhibits an absorption ranging from 550 nm and up to 750 nm and its blend with PC71BM afforded polymer solar cells with an initial energy conversion efficiency of 7.40%.[45] The fluorine effect is also demonstrated in a recently reported alternating copolymer with thiophene–tetrafluorophenyl–thiophene and furan-flanked diketopyrrolopyrrole moieties (PDPPF–TFPT) that exhibits a balanced ambipolar behavior as required for applications in organic thin-film transistors (Scheme 7).[46]

In an orthogonal synthetic approach a series of AB-alternating, side-chain-functionalized poly(thiophene) analogs were designed aiming to selectively localize at the interface between regioregular poly(3-hexylthiophene) (rr-P3HT) and PCnBM ($n = 61$, 71) in BHJ solar cells. The side chains of every other repeat unit in those polythiophenes (Scheme 8) contained various terminal aromatic moieties and were prepared via GRIM polymerization of dithiophenes carrying the side-chain functionality in one of the thiophene rings as shown in Scheme 8.[47] Pentafluorophenoxy-containing polymer was the most effective side-chain-functionalized additive and yielded a 28% increase in PCE when incorporated into a 75 nm thick rr-P3HT/PC61BM BHJ at a 0.25 wt% loading. Moreover,



Scheme 7. Examples of semiconducting polymers bearing fluorine substituents.[45,46]

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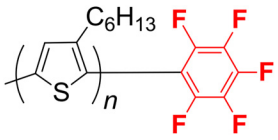


Scheme 8. AB-alternating, side-chain-functionalized poly(thiophene)s prepared from a dithiophene functionalized monomer.[47]

devices with 220 nm thick BHJs containing 0.25 wt% that perfluorophenyl-functionalized rr-P3HT displayed PCE values of up to 5.3% which was a 30% PCE increase over a control device lacking the additive. In fact, when the perfluorophenyl-alternating rr-P3HT was compared with analogs but random regioregular, homopolymeric or random regiorandom structures it was found that only the AB-alternating regioregular polymer lead to increased charge-carrier lifetimes versus a reference cell.

Recently, perfluorophenyl ω-end functionalized P3HT was prepared by the in situ addition of perfluorophenyl magnesium bromine as end-capper of the "living" bromine chain ends (Scheme 9).

A novel functionalization-sensitization route for the decoration of TiO_2 nanoparticles (NPs) and or nanoparticulate TiO_2 thin films with polymeric dyes was then demonstrated via the creation of stable and non-hydrolysable Ti–O–C carbon bonds.[48]

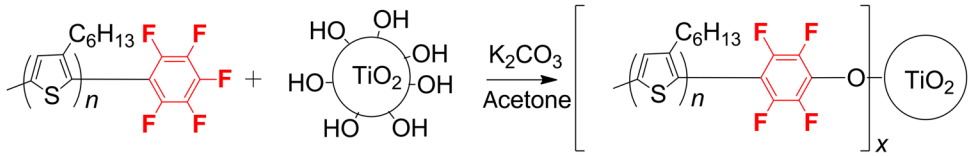


Scheme 9. Introduction of the end perfluorophenyl group.[48]

These were realized via an etherification analog reaction of perfluorophenyl-functionalized organic light-absorbing dyes with the hydroxyl groups located onto the TiO_2 surface. The initial experiments and the proof of concept were performed using simple monomeric perfluorophenyl-functionalized quinolines. Thereafter the methodology was extended to the perfluorophenyl-functionalized rr-P3HT as can be seen in Scheme 10.

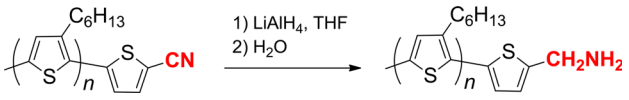
A photoluminescence (PL) quenching was detected for the hybrid rr-P3HT-5F-TiO_2 NPs after excitation at the absorption maximum of rr-P3HT. This was attributed to the covalent attachment of the rr-P3HT-5F moieties onto the TiO_2 NPs allowing the efficient electronic interactions between the two species. rr-P3HT-5F-sensitized TiO_2 photoanodes were also prepared under analogs conditions at which the stability of the created Ti–O–C bonds was prominent even after extensive washing with organic and aqueous media. The rr-P3HT-5F-sensitized TiO_2 photoanodes were tested and found functional in dye-sensitized solar cells (DSSCs) and in photoelectrochemical cells for water splitting under alkaline conditions. The same methodology is applicable also for low-band gap alternating electron donors carrying perfluorophenyl moieties at their chain ends.[49]

Another multi-practical functionality is the amino moiety. For instance, an amino-end-functional polythiophene was employed as CdSe nanocrystals (NCs) dispersant and thus, affording nanocomposites with favorable morphology for use in P3HT/CdSe



Scheme 10. Modification of TiO_2 surface with perfluorophenyl-functionalized rr-P3HT.[48]

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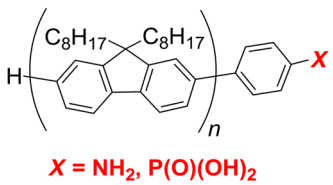


Scheme 11. Synthesis of P3HT with amino-end functionality.[50]

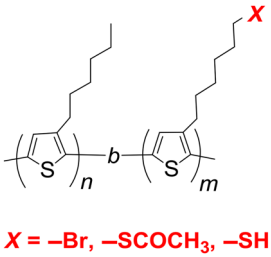
hybrid solar cells. Stille coupling reaction of P3HT carrying a bromine end-group with an organotin thiophene compound bearing a cyano group afforded polymer (a), which was transformed into (b) after reduction with $LiAlH_4$ (Scheme 11).[50]

Since hybrid NPs comprised of inorganic semiconductor quantum dots (QDs) and organic semiconductor-conjugated polymers have nowadays gained considerable interest, other semiconductors besides poly(thiophene)s, have also been employed after their functionalization for QDs' dispersion.[51,52] Thus, side amino-functionalized polyfluorenes onto CdSe/ZnS QDs by replacing the initial pyridine ligands used in the QDs synthesis with the polyfluorene derivatives have been reported.[53] Moreover, functionalized ligands during the QD synthesis can be used to subsequently polymerize from- or attach to- a pre-synthesized polymer to the QD surface ("grafting from" or "grafting to" approaches). Emrick et al. reported the "grafting from" route where a bromine functionalized ligand was used during QD synthesis and then oligo(p-phenylene-vinylene) tri- and tetramers were built onto the CdSe QDs.[54] In another report, hybrid particles composed of an inorganic semiconductor NC with a shell of organic semiconductor ligands were prepared directly by high-temperature synthesis. Functionalized fluorenes with amine or phosphonic acid end-groups for binding to the inorganic interface were synthesized by Suzuki–Miyaura coupling polymerization using novel three-coordinated Pd(II) complexes as initiators (Scheme 12).[55]

In an analog approach toward functionalized P3HTs, phosphonic ester, pyridine, protected thiol, and protected phenol end-groups functionalized air-stable Ni initiators were employed. These functional groups were used to synthesize hybrid materials consisting of different NPs anchored with P3HT, such as metal oxides (e.g., superparamagnetic Fe_3O_4) decorated using the phosphonic ester, CdSe/ZnS QDs combined with the pyridine, whereas noble-metals- (Au-) based NPs interacted with the thiol and phenol groups.[56] A recent comprehensive review on the attachment of semiconducting species onto inorganic substrates can provide more detailed information onto this inorganic-conjugated polymer hybrids formation.[57]



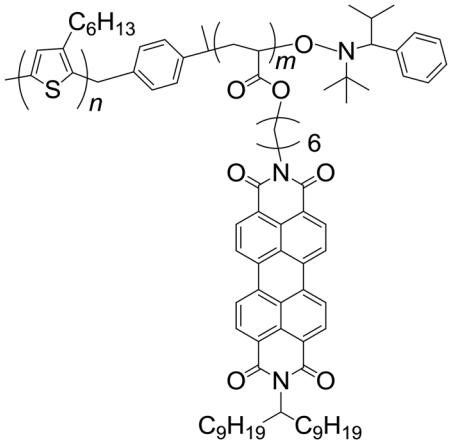
Scheme 12. Fuctionalized polyfluorenes PF-C_6H_4-NH_2 and PF-C_6H_4-P(O)$(OH)_2$.[55]



Scheme 13. Preparation of block copolymer of side functionalized P3HT via the GRIM polymerization.[58]

A discrete block copolymer of side-functionalized P3HT has been presented which is synthesized by sequential addition of the net alkyl-thiophene and the bromine-functionalized alkyl-thiophene monomer at various ratios, via the GRIM polymerization (Scheme 13). The bromine groups were then transformed to thiol-functionalities and the block copolymers were studied in respect to electronic interactions with non-toxic bismuth sulfide (Bi_2S_3) NCs showing an efficient charge transfer between the P3HT-SH and the Bi_2S_3 NCs. Improved PV performance was obtained from the P3HT-SH/Bi_2S_3 NCs cells versus the plain P3HT/Bi_2S_3 NCs ones.[58]

The most widely used non-fullerene acceptor is perylene bisdiimide (PDI), due to its relatively high electron affinity, good electron mobility, and strong absorption of visible light. In most representative cases, PDI containing donor–acceptor copolymers have been prepared employing initiator functionalized P3HT rods. The Thelakkat group after initial reports on a triphenylamine–PDI coil–coil block copolymer[59–61] extended their approach to polythiophene block copolymers bearing PDI coil blocks (Scheme 14).[62] Analogs block copolymers were also reported by other groups[32,63,64] consisting of a hole-transporting block of P3HT and an electron-transporting block of PDI-pendant polyacrylates.



Scheme 14. P3HT-block-poly(perylene bisimide acrylate) donor–acceptor copolymer.[62]

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Hybrid nanostructures of functional semiconducting polymers with carbon nanostructures

As above mentioned, the great advancements for the preparation of new more efficient electron donors based on their optimum chemical structure design mainly using electron-donating and electron-accepting building blocks along the main chain in order to modulate the electronic properties and the effective band gap, resulted in significant efficiency increase. Furthermore, the development of new fullerene derivatives also contributed to the efficiency increase even for systems that seemed to have leveled off like in the P3HT:ICBA case. However, the rational design and control of the morphology of these systems proved to be trickier and up to now empirical methods like annealing seem more efficient than a knowledge-gained approach based on the deeper understanding of the exact parameters that correlate the morphological behavior of such systems.

To this end the design and preparation of hybrid structures can significantly contribute both from the modulation of energy levels and also by controlling the morphology of the active layer. Thus, electron donor–fullerene hybrid structures and electron donor–CNT hybrids have been created. The different synthetic methodologies used, resulted in hybrids with various connection chemistries between the semiconducting species and the carbon nanostructures. This was initially necessary to prove the synthetic feasibility and the influence of the hybrids on the active layer morphology control and stabilization. Thereafter more controlled ways of chemical connection in the sense of direct attachment of the semiconducting species to the carbon nanostructure became available.

Semiconducting polymer/CNTs hybrids

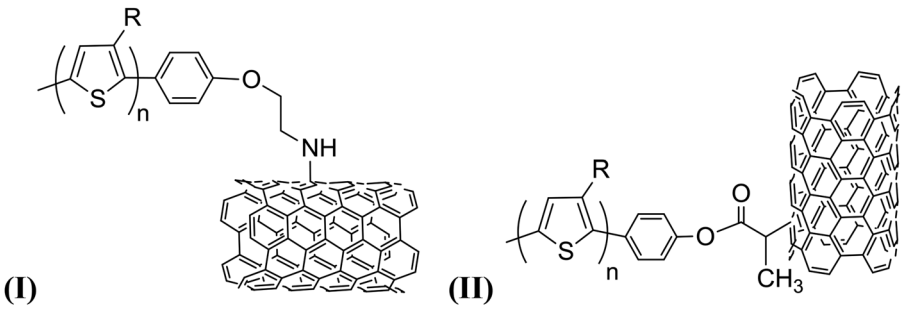
CNTs have been used as the transport medium in BHJ solar cells and as mobility enhancers within TFTs. CNTs, particularly semiconducting single-wall carbon nanotubes (SWCNTs) have attracted great scientific interests owing to their extraordinary charge carrier mobility and their nanometer dimensions that enable charge transport along the nanotubes long axis with reduced charge recombination when applied into OPVs.

The preparation of semiconducting polymer/CNT hybrid materials refers to the attachment of the semiconductor by one or more connecting sites onto the CNTs surface. There are of course several studies at which the non-covalent interaction and un-bundling of CNTs with a semiconducting polymer is described, but these do not constitute the development of hybrid materials.

The two major pathways for the decoration of CNTs with polymeric materials are the "grafting from" or "grafting to" routes. Meaning either polymerizing the desired monomer from initiating sites previously created onto the surface of CNTs or attaching a pre-developed polymeric entity carrying the appropriate functional group onto CNTs. "Grafting to"[65] or "grafting from"[66] techniques have also been used for the conventional polymer modification of nanotubes. In order to prevent the disruption of p-conjugation, various modifications[67,68] that allow weak functionalization of the SWNTs, resulting in the lowest possible distortion of their electronic properties, can be used.[69,70]

In cases that the targeted application of the modified SWCNTs is their use as optoelectronic materials, attachment of semiconducting units is of utmost importance trying to increase the processability and applicability of nanotubes within the active layers of OPVs or as current collecting electrodes. Recent advances on the enrichment of the semiconducting character in SWCNTs expand the perspective for the use of such materials in PV applications. In these cases, the control over the electronic properties in the semiconducting SWCNTs is combined with the solubility improvement by simply using semiconducting organic species as covalent SWCNTs modifiers.

As an example Stefopoulos et al.[71] presented hybrid materials consisting of the electron-donating rr-P3OT covalently attached to SWCNTs using either hydroxyl decorated SWCNTs and hydroxyl ω-end functionalized rr-P3OT under a Mitsunobu-type etherification reaction (hybrid I, Scheme 15) or 2-chloropropionyl phenyl ester ω-end functionalized rr-P3OT and net SWCNTs under atom-transfer radical addition (ATRA) conditions (hybrid II, Scheme 15). The reported hybrids presented dispersability and processability in common organic solvents, and at the same time combination of both counterparts' properties. Interestingly PL quenching of the rr-P3OT was observed for the hybrid materials in their solid thin-film state, providing proof of the energy transfer from the polymeric semiconductor to the CNT (Fig. 2).



Scheme 15. Hybrid materials of SWCNTs with hydroxyl ω-end functionalized rr-P3OT (I) and 2-chloropropionyl phenyl ester ω-end functionalized rr-P3OT (II).[71]

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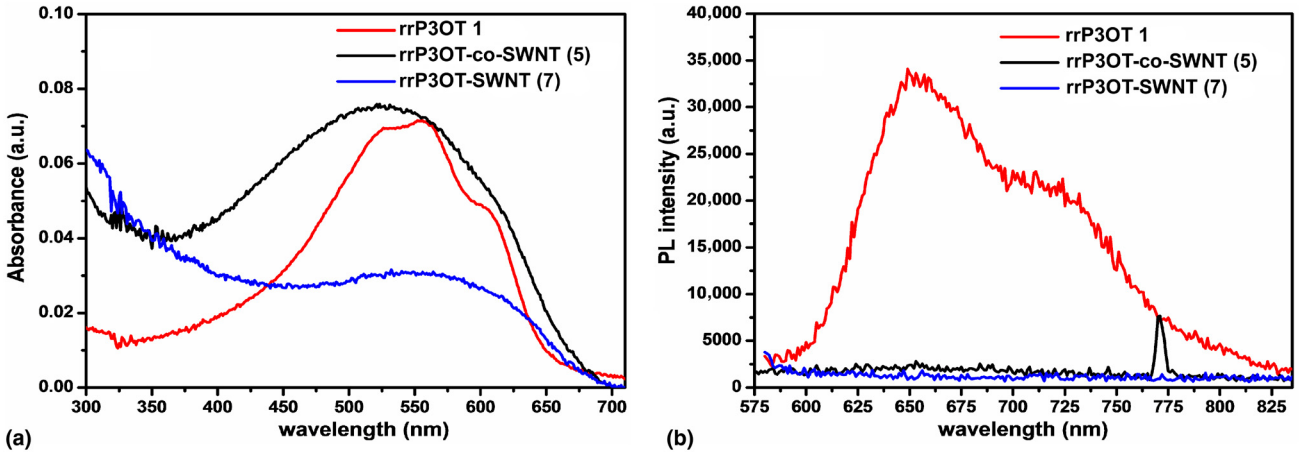


Figure 2. UV–vis (a) and PL (b) spectra of rr-P3OT and of the rr-P3OT–SWCNTs hybrids (I) and (II) shown in Scheme 15, in the thin-film state. Reproduced from Ref. 71 by permission of John Wiley and Sons 2008.

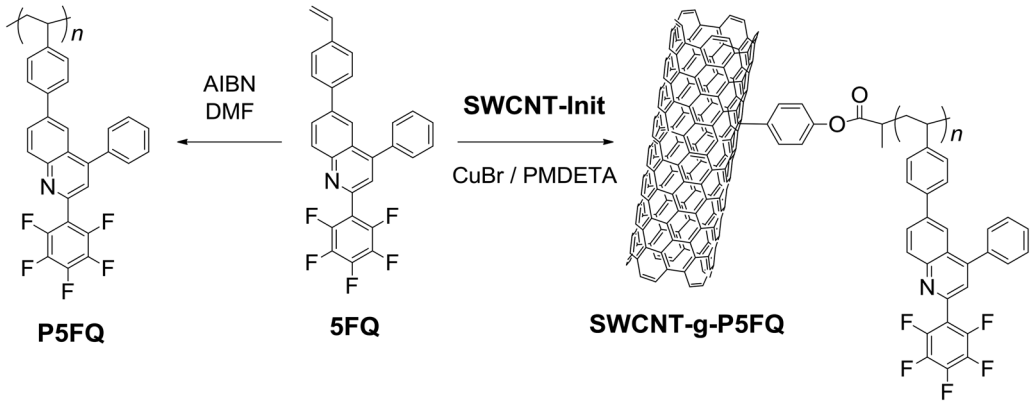
Electron-accepting poly(vinylphenyl-phenylquinoline) was employed for the functionalization of SWCNTs via the "grafting from" technique.[72] Polymerization of the vinylphenyl-phenylquinoline monomer onto properly modified SWCNTs using atom-transfer radical polymerization (ATRP) conditions resulted in efficient grafting of the optically active oligomeric chains onto the nanotubes.

In a continuation of the semiconducting polymer modification of SWCNTs, our group used poly(vinylphenyl perfluorophenyl-phenylquinoline) (P5FQ) for the preparation of the hybrid SWCNTs-graft-P5FQ (Scheme 16).[73] The "grafting from" method was employed also in that case were ATRP initiating sites were created onto the SWCNTs surface that were used for polymerizing the vinyl perfluorophenyl-quinoline monomer.

As a step further, our group developed even more hybrid materials by functionalizing SWCNTs with different semiconducting vinyl quinoline monomers bearing electron-accepting groups or a ruthenium–quinoline complex. From the band diagrams of the pristine and modified nanotubes it is evident that the strongest charge transfer occurred in the case of the metal complex derivative in agreement with the results of the Raman studies, while the same complex had the highest LUMO energy. The attachment of the quinoline molecules in the SWCNTs body led to hybrid materials with HOMO positions in between the HOMO positions of the net components (Fig. 3).[74]

Semiconducting polymer/fullerene hybrids

As already described a well-investigated approach toward controlling the morphology at the nanometer and stabilizing the nanophase separation of conjugated polymer–fullerene BHJ solar cells over the long-term is the incorporation in the active layer of diblock copolymers acting as compatibilizers that bear distinct blocks of the electron donor and of the electron-accepting fullerene. Such diblock copolymers act as compatibilizers similarly to the typical immiscible or partially miscible polymer blends compatibilization. The interfacial tension between the polymer donor and fullerene acceptor phases is reduced and their aggregation over larger domains is also suppressed.



Scheme 16. Preparation of P5FQ and its anchoring onto SWCNTs.[73]

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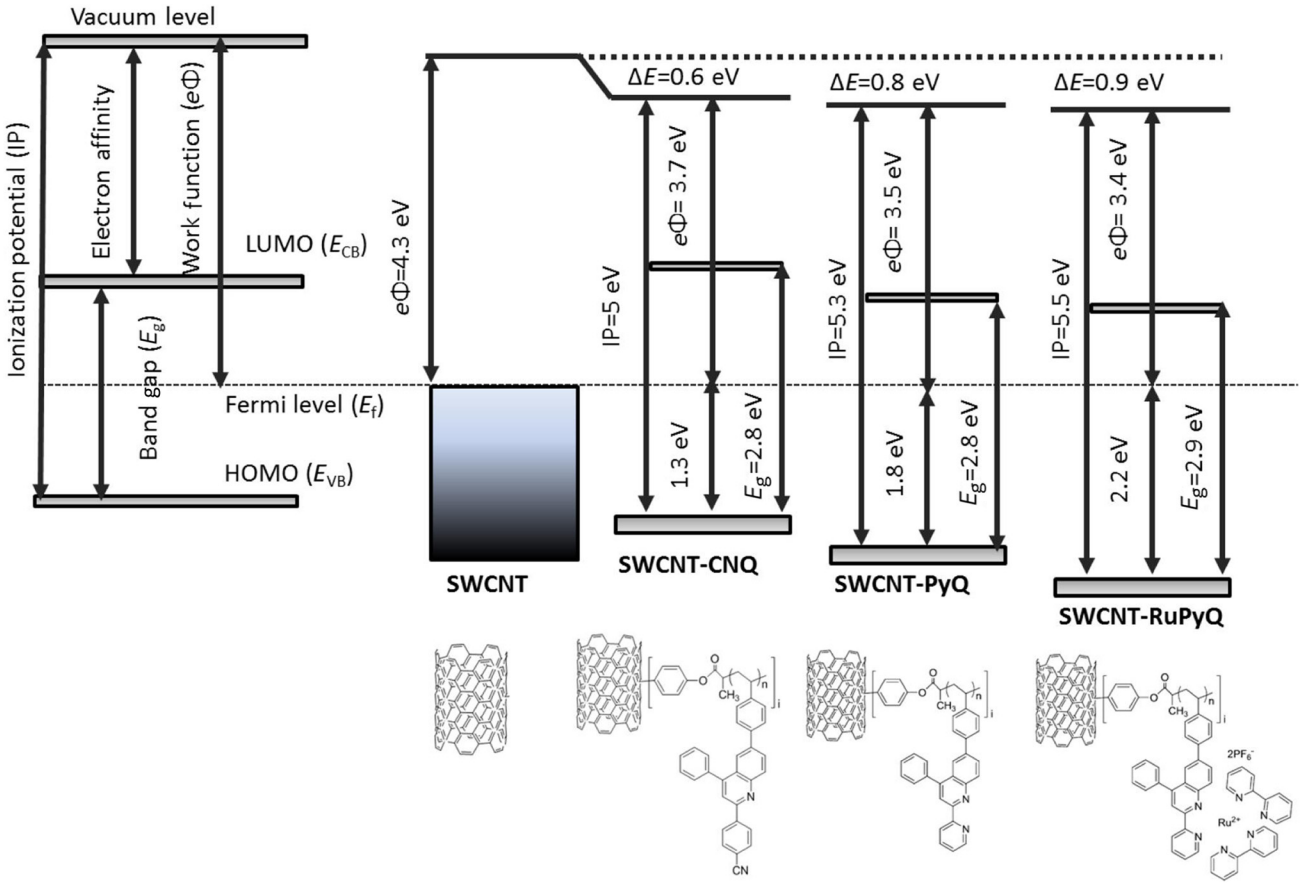


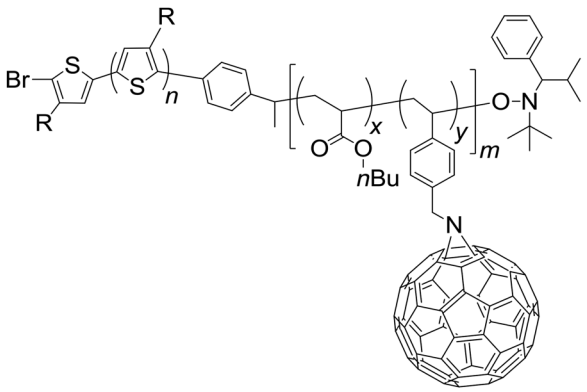
Figure 3. Schematic diagram of the pristine SWCNTs and the hybrid materials energy bands measured by UPS and energy gaps calculated from the UV–vis–NIR spectra and the corresponding LUMO positions. Adapted with permission from Ref. 74, copyright (2013) American Chemical Society.

In the first attempts functionalized PPVs and P3ATs were used as the donor blocks and the fullerene species were covalently attached on flexible polymeric blocks. The first donor–acceptor block copolymer with good electronic properties was synthesized by the group of Hadziioannou,[75] using a PPV electron donor block as macroinitiator for the nitroxide mediated radical polymerization (NMRP) of styrene and chlorostyrene. Then the synthesized block copolymer was modified with fullerenes via atom transfer radical addition (ATRA).

This structure was modified several times in the years to follow, in order to improve the synthetic route.[76,77] It was found that the electron mobility of the hybrid materials was increased due to the incorporation of the C60 units, but still remained below the electron mobility of net PCBM. Also even though C60 was immobilized onto the coil copolymeric block, crystallinity problems were still observed. Nevertheless, the fact that the hybrid copolymer gave better performance than the polymers themselves in blend, reinforced the idea of using conjugated rod–coil hybrid block copolymers in PV devices.

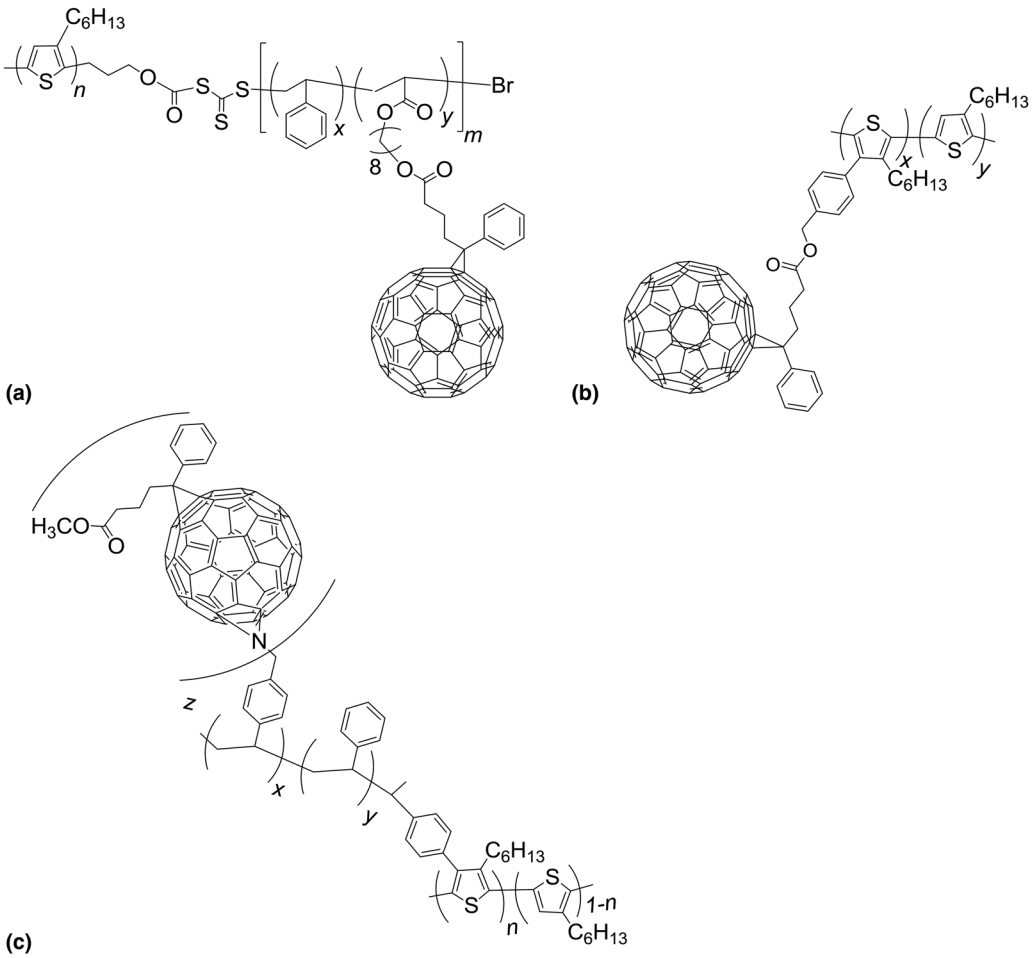
Thereafter most research groups,[78–82] synthesized similar hybrid copolymers using poly(3-alkylthiophene), as the semiconducting rod block Scheme 17. In most cases, the morphology of the active layer was significantly improved when employing the hybrid materials; however, the device performance remained unaltered.

In order to improve the morphology as well as to increase the performance of the device some research groups focused



Scheme 17. A hybrid copolymer consisting of a poly(3-alkylthiophene) block and of flexible *n*-butyl acrylate and styrene-C60 coils.[79]

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Scheme 18. Poly(thiophene) hybrid copolymers carrying $PC_{60}BM$ units [(a)[86], (b)[88], (c)[84]].

on the development of hybrid copolymers bearing immobilized units of PCBM,[83–88] instead of C60. Scheme 18 shows some representative hybrid copolymeric structures prepared by creating initiators at the end group of poly(thiophene)s, or by modifying the side chains of the polythiophene ring in the 4 position. When the well-defined rod–coil block copolymer of Scheme 18(a) was used as "surfactant" of the P3HT:PCBM blend, the control of the interface morphology of the donor–acceptor phase domains within the composite resulted in an improvement of the efficiency with respect to the analogous solar cell fabricated without the "surfactant".[86]

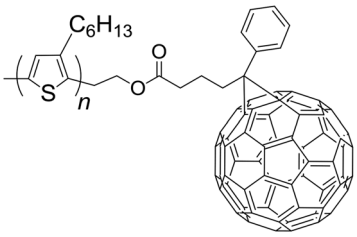
Another interesting approach was the synthesis of polythiophene-b-[poly(4-vinylpyridine) (P4VP)]copolymers, since P4VP is known to associate non-covalently with PCBM,[89,90] based on the fact that each molecule of PCBM can form non-covalent bonds with up to six molecules of 4VP.[91] In the case where the copolymer was used as the donor and complexating agent in blends with PCBM, only moderate yields in PV devices were obtained.[89] On the other hand, when a P3HT-b-P4VP copolymer was incorporated as a compatibilizer in P3HT:PCBM blends, in low fraction volumes, high-efficient solar cells were obtained without necessitating any additional thermal or solvent annealing of the active layer.[90]

However, the above-described cases of diblock copolymers compatibilizer having P3HT rod and flexible coils at which the fullerenes are attached require multi-staged post-polymerization reactions constituting their practicality quite limited. Furthermore, the large volumes of the insulating coil blocks cause reduce charge carrier transport in the BHJ devices.

As a possible solution to the complexity and practicality of hybrid polythiophene compatibilizers, a more simple C60-end-capped poly(3-hexylthiophene) (P3HT-C60) (Scheme 19) was reported.[83,92]

When this end-capped polymer was used as a compatibilizer for P3HT/PCBM blends the bicontinuous and nanometre-scale film morphology was preserved even after prolonged annealing times, and as a result, the P3HT/PCBM/P3HT-C60 BHJ solar cells exhibited the excellent long-term thermal stability of device performance Fig. 4.[83] Self-assembly of the P3HT-C60 end-capped polymer resulted in nanostructures with well-defined donor–acceptor interfaces depending on the solvent employed as schematically shown in Fig. 5.[92–94]

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Scheme 19. C60-end-capped poly(3-hexyl thiophene).[83,92]

Non-conjugated connecting bridges were employed in the above cases for the attachment of the organic part onto the carbon nanostructure. On the other hand, if a conjugated bridge is inserted in-between the semiconductor and the carbon nanostructure through a "direct" attachment the electronic interactions of the two counterparts should be enhanced leading to unique integrated properties for the final hybrids.

The perfluorophenyl functionality allows such a direct attachment through the transformation of one of the fluorine atoms to a stable azide and subsequent [3 + 2]-cycloaddition onto the fullerene's surface. 1,6-Azo bridged carbon nanostructure–organic semiconducting hybrids are created via this route.[95–99] This direct coupling of fullerenes onto semiconducting copolymers bearing electron-accepting poly(vinylphenyl perfluorophenyl-quinoline) blocks and electron-donating regioregular poly(3-alkyl thiophene) blocks was reported by Kakogianni et al. (Scheme 20).[40] As can be seen in Fig. 6(b) films of P3OT-(P5FQ-N-PCBM) prepared using *o*-DCB presented smaller nanophase segregated domains, than those from THF [Fig. 6(a)] owing to the enhanced solubility of the polymeric and of the fullerene moieties.

Polythiophene with pendant cyclopentadienyl groups was synthesized by employing GRIM polymerization and post-polymerization modifications and was finally conjugated to fullerenes (C60, PCBM, ICBA) via a Diels–Alder reaction (Scheme 21). The covalent P3HT–fullerenes hybrids formed smoother aggregation-free films with fine lamellae compared with the respective P3HT/fullerenes physical blends.[100]

In a different approach the synthesis of hybrid polythiophene–C60 copolymers was accomplished by the copolymerization of a fullerene comonomer and difunctional P3HT rods as the second comonomer. Interesting highly linear donor–acceptor wire-like structures were obtained under specific substrates and casting, annealing conditions.[101] In a more defined manner and only quite recently a novel approach has been reported for the preparation of alternating polythiophene–fullerene hybrids at which the fullerene moiety is introduced as a comonomer during the polymerization reaction. Oligothiophene/fullerene alternating copolymers were prepared via condensation of dialdehyde functionalized oligothiophene segments of 15–30 r.u. and aromatic diamines carrying the fullerene unit (Scheme 22).[102]

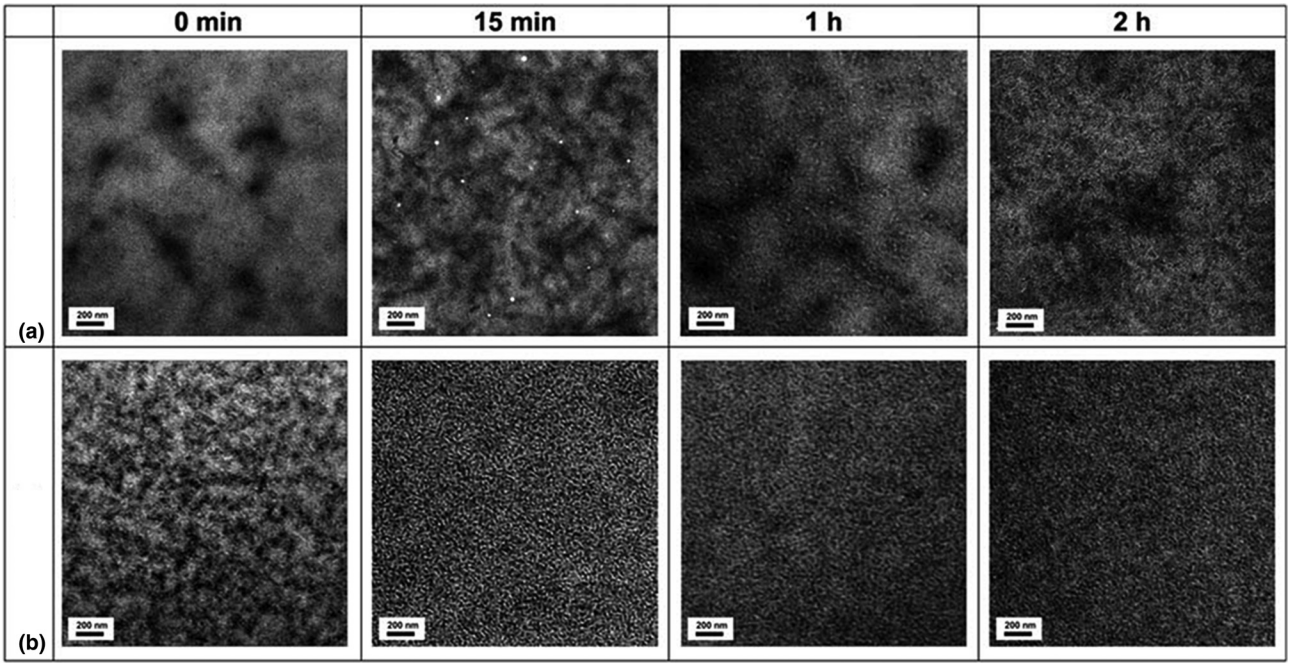


Figure 4. TEM images of (a) the standard P3HT/PCBM and (b) P3HT/PCBM/P3HT-C60 composite film with the addition of 2.5 wt% P3HT-C60 as a function of annealing time at 150 °C. Reproduced Ref. 83 with permission of The Royal Society of Chemistry.

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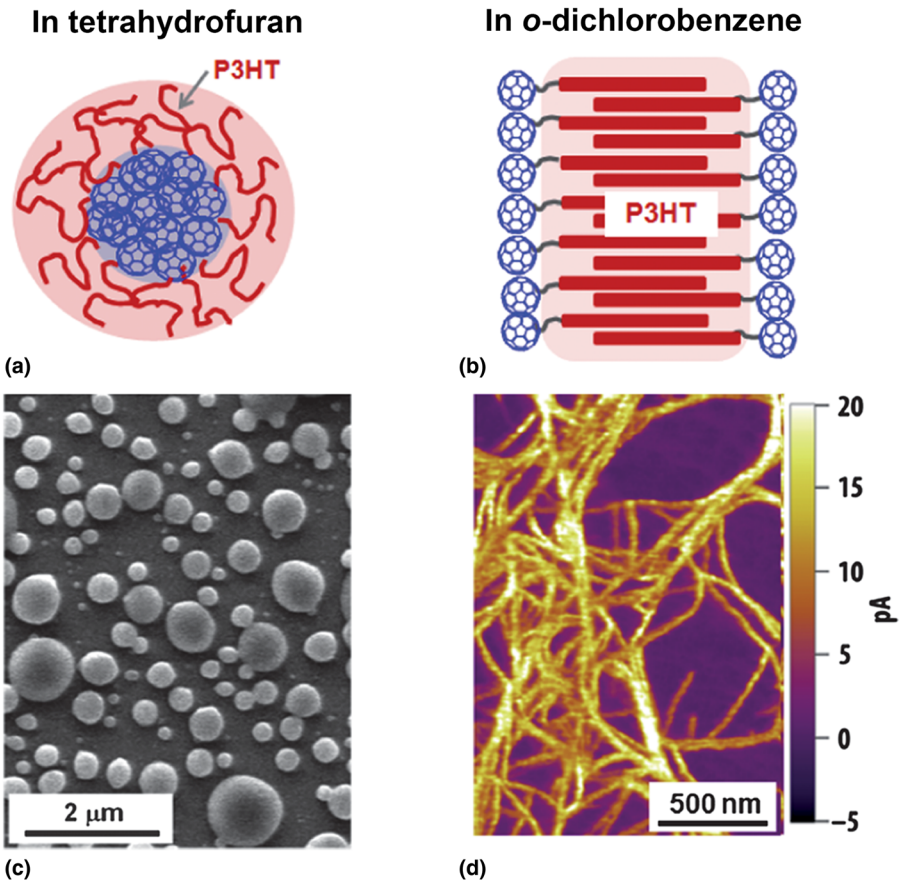


Figure 5. Schematic representations of spherical (a) and fibrillar (b) nanostructures formed by P3HT-C60 of Scheme 19 where $n = 30$. (c) A scanning electron microscope (SEM) image of THF-cast film of P3HT-C60 shows spherical aggregates with varying sizes. (d) A photocurrent image collected at 0 V from *o*-DCB-cast film of P3HT-C60 showed well-resolved fibrillar structures with high contrast versus the background signal. Reproduced Ref. 94 with permission of The Royal Society of Chemistry.

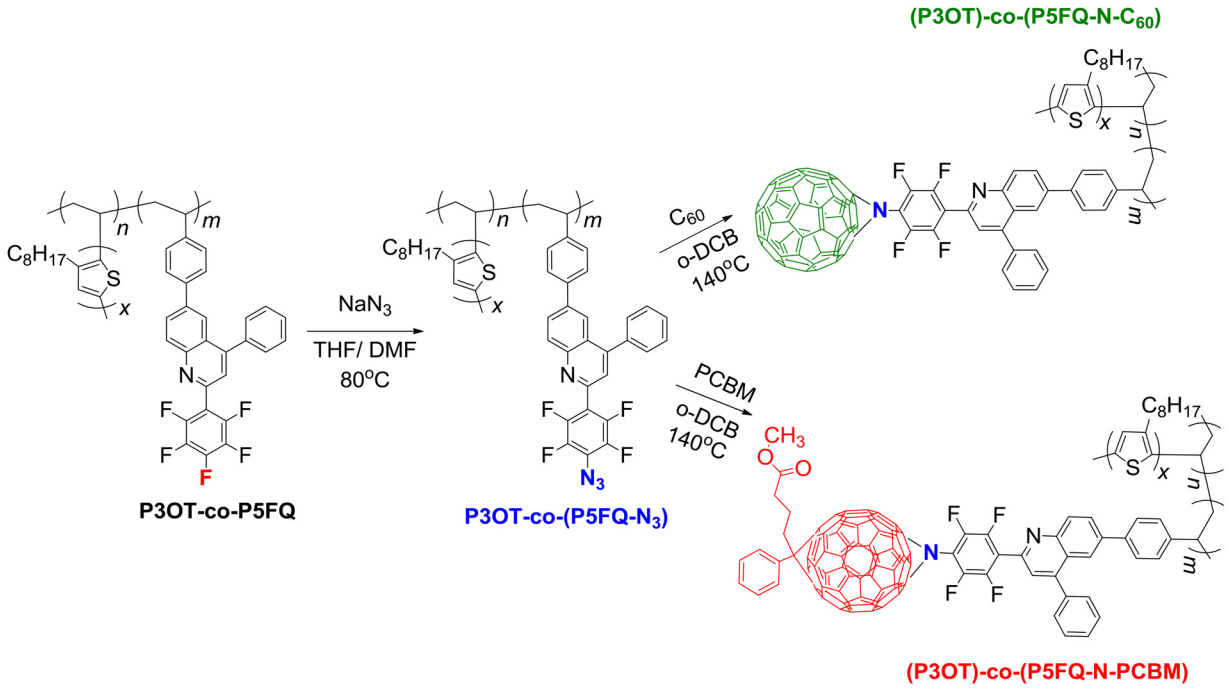
Future prospects in applications of functional semiconducting polymers and hybrid organic materials with carbon nanostructures or inorganics

The advantages of organic conjugated semiconducting polymers such as versatile structural design, optoelectronic properties determined by the exact chemical structure, lightweight, mechanical strength, and flexibility have made possible enormous technological breakthroughs in the field of organic electronics. Nevertheless, for the realization of competitive technologies with broad commercialization potential requires well-defined materials and devices with "on-demand" properties, stability, and long-lasting operation under all environmental conditions and every day mistreatments. In general, strong limitations are the lack of accurate predictions over the active layer's morphology and properties and therefore the device's efficiency and stability through the design of new semiconductors. Through the various ways to manipulate the polymers' characteristics in terms of chemical structure, nanophase ordering, miscibility with complementary materials (polymeric, carbon-based nanostructures, and inorganics) and optoelectronic properties it is expected that eventually all shortcomings will come to a "happy-ending". Obviously this can be achieved only through interdisciplinary work in material synthesis, morphology control, and device design and fabrication.

As seen from the above sections, polymer chemists have come up with many, different polymer structures bearing functionalities that can modulate the optoelectronic properties and lead to controlled or even, in some cases, stabilized morphologies. Semiconducting polymers carrying functional units offer endless possibilities for the combination of moieties with different properties and with defined architectures leading to self-organized structures with domains in the nanometer scale.

The availability of the various synthetic methodologies for the functionalization of polymeric semiconducting units together with the realization of the potentiality of the carbon-based hybrid nanostructures also paved the way for the development of semiconducting carbon nanostructure hybrids of various architectures. This recent trend in the combination of functional polymers with carbon-based nanostructures

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Scheme 20. Modified fullerenes with semiconducting copolymers bearing electron-accepting poly(vinylphenyl perfluorophenyl-quinoline) and electron-donating regioregular poly(3-alkyl thiophene) blocks.[40]

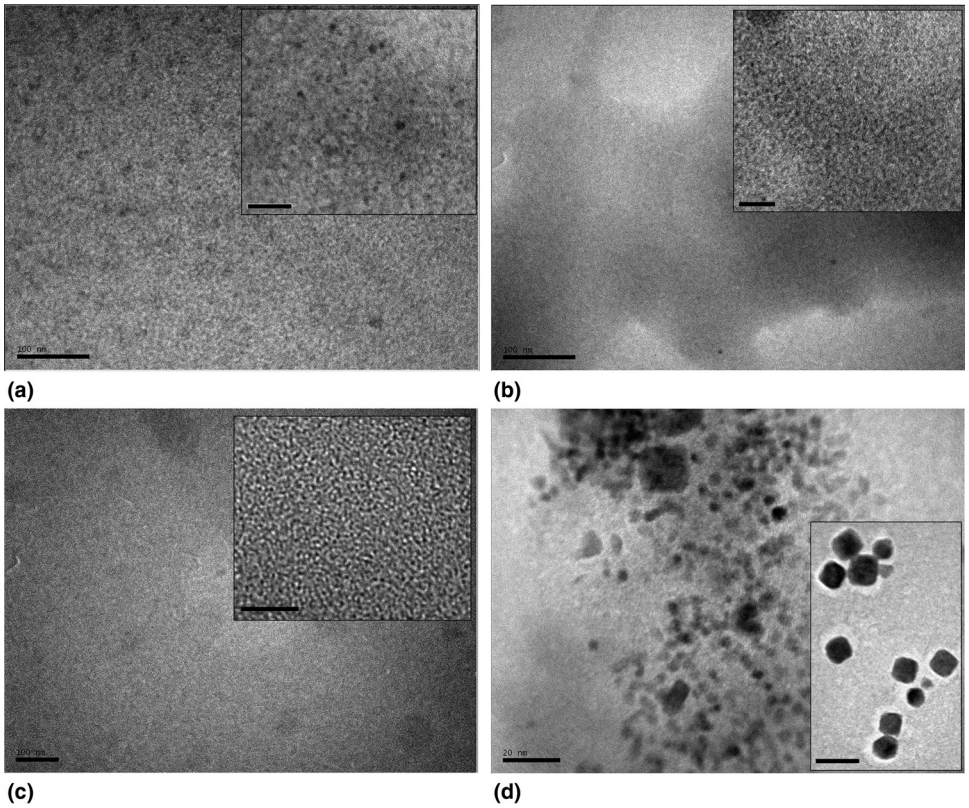
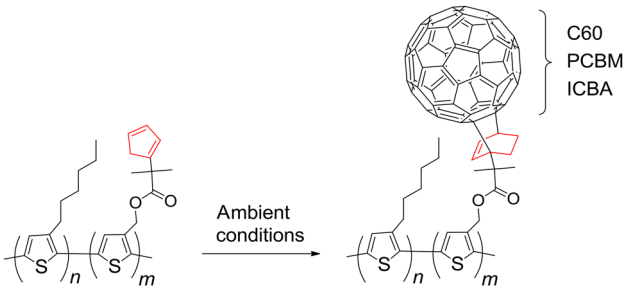


Figure 6. TEM images of unstained P3OT-(P5FQ-N-PCBM) (from Scheme 20) (a) using THF and (b) using *o*-DCB; (c) of P3OT–PF5FQ using *o*-DCB (scale bar 100 nm). The insets in (a) –(c) show higher magnifications with the scale bar corresponding to 20 nm; (d) shows the TEM image of a P3OT-P5FQ/PCBM blend and of the net PCBM (inset, 20 nm scale bar) both using *o*-DCB. Reproduced Ref. 40 with permission of The Royal Society of Chemistry.

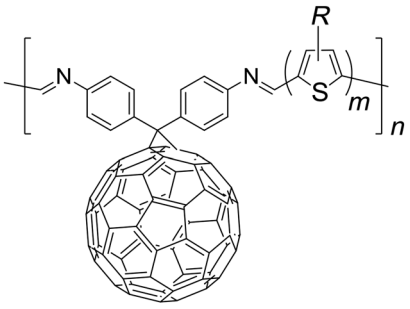
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Scheme 21. Polythiophenes with cyclopentadienyl pendant groups and covalent hybrids with different fullerenes, fabricated via Diels–Alder ligation under ambient conditions.[100]

such as fullerene derivatives and CNTs extend the applicability of semiconducting polymers and copolymers toward multifunctional polymeric hybrid materials. For example, semiconducting polymer-modified carbon nanostructures show great promise for optoelectronic applications and especially for OPVs due to their dual functionalities, both of the semiconducting species and of the fullerene or CNTs derivatives. Different synthetic approaches have been followed using a variety of chemistries for the covalent attachment of the functionalized semiconducting species onto carbon nanostructures. Recent advancements on the direct coupling of the functionalized semiconductors onto the carbon nanostructures open new ways for the synthetic consideration of these hybrid materials and enable their exploitation in a wide range of applications. The direct connection of the two moieties and the hybrids eventual distribution to the donor–acceptor interface, provide the means for better nanophase and interface stabilization and control of the nanodomains dimensions. These hybrids resemble the block copolymers characteristics and can eventually influence, control, and finally stabilize the morphology of blends constituting the net components.

By a chemically straightforward synthesis with the ability to prepare materials at any requested amount, a prerequisite to the realistic use of hybrid materials has been eventually fulfilled. The existence of functionalized semiconducting species with different functional groups also opens the way of their attachment to other nanomaterials such as inorganic semiconductors providing thus potential materials for DSSCs.



Scheme 22. Fullerene alternating copolymer prepared from dialdehyde oligothiophenes.[102]

Acknowledgments

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References

1. A.J. Heeger: Semiconducting and metallic polymers: the fourth generation of polymeric materials (Nobel Lecture). *Angew. Chem., Int. Ed.* **40**, 2591–2611 (2001).
2. J.E. Carle, M. Helgesen, M.V. Madsen, E. Bundgaard, and F.C. Krebs: Upscaling from single cells to modules–fabrication of vacuum- and ITO-free polymer solar cells on flexible substrates with long lifetime. *J. Mater. Chem. C* **2**, 1290–1297 (2014).
3. Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao: Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. *Nat. Photonics* **6**, 591–595 (2012).
4. P.-L.T. Boudreault, A. Najari, and M. Leclerc: Processable low-bandgap polymers for photovoltaic applications. *Chem. Mater.* **23**, 456–469 (2011).
5. S.Y. Hong, M. Kertesz, Y.S. Lee, and O.K. Kim: Geometrical and electronic structures of a benzimidazobenzophenanthroline-type ladder polymer (BBL). *Macromolecules* **25**, 5424–5429 (1992).
6. A. Babel and S.A. Jenekhe: High electron mobility in ladder polymer field-effect transistors. *J. Am. Chem. Soc.* **125**, 13656–13657 (2003).
7. M.M. Alam and S.A. Jenekhe: Efficient solar cells from layered nanostructures of donor and acceptor conjugated polymers. *Chem. Mater.* **16**, 4647–4656 (2004).
8. M. Jeffries-EL and R.D. McCullough: 'Regioregular Polythiophenes', Chapter 9 in T.A. Skotheim and J. Reynolds (eds), *Handbook of Conducting Polymers*, 3rd ed. (CRC Press, LLC, Boca Raton, FL, 2007), pp. 1–49.
9. I.F. Perepichka and D.F. Perepichka (eds): *Handbook of Thiophene Based Materials: Applications in Organic Electronics and Photonics, Volume One: Synthesis and Theory* (John Wiley & Sons, Chichester, 2009).
10. R.D. McCullough: The chemistry of conducting polythiophenes. *Adv. Mater.* **10**, 93–116 (1998).
11. R.S. Loewe, P.C. Ewbank, J. Liu, L. Zhai, and R.D. McCullough: Regioregular, head-to-tail coupled poly(3-alkylthiophenes) made easy by the grim method: investigation of the reaction and the origin of regioselectivity. *Macromolecules* **34**, 4324–4333 (2001).
12. R. Miyakoshi, A. Yokoyama, and T. Yokozawa: Catalyst-transfer polycondensation. Mechanism of Ni-catalyzed chain-growth polymerization leading to well-defined poly(3-hexylthiophene). *J. Am. Chem. Soc.* **127**, 17542–17547 (2005).
13. T. Beryozkina, V. Senkovskyy, E. Kaul, and A. Kiriy: Kumada catalyst-transfer polycondensation of thiophene-based oligomers: robustness of a chain-growth mechanism. *Macromolecules* **41**, 7817–7823 (2008).
14. V. Senkovskyy, M. Sommer, R. Tkachov, H. Komber, W.T.S. Huck, and A. Kiriy: Convenient route to initiate kumada catalyst-transfer polycondensation using Ni(dppe)Cl_2 or Ni(dppp)Cl_2 and sterically hindered grignard compounds. *Macromolecules* **43**, 10157–10161 (2010).
15. A. Kiriy, V. Senkovskyy, and M. Sommer: Kumada catalyst-transfer polycondensation: mechanism, opportunities, and challenges. *Macromol. Rapid Commun.* **32**, 1503–1517 (2011).
16. J.S. Liu and R.D. McCullough: End group modification of regioregular polythiophene through postpolymerization functionalization. *Macromolecules* **35**, 9882–9889 (2002).

https://doi.org/10.1557/mrc.2015.42 Published online by Cambridge University Press

17. Y. Li, G. Vamvounis, J. Yu, and S. Holdcroft: A novel and versatile methodology for functionalization of conjugated polymers. Transformation of poly(3-bromo-4-hexylthiophene) via palladium-catalyzed coupling chemistry. *Macromolecules* **34**, 3130–3132 (2001).
18. M.C. Stefan, M.P. Bhatt, P. Sista, and H.D. Magurudeniya: Grignard metathesis (GRIM) polymerization for the synthesis of conjugated block copolymers containing regioregular poly(3-hexylthiophene). *Polym. Chem.* **3**, 1693–1701 (2012).
19. S.P. Economopoulos, C.L. Chochos, V.G. Gregoriou, J.K. Kallitsis, S. Barrau, and G. Hadziioannou: Novel brush-type copolymers bearing thiophene backbone and side chain quinoline blocks. Synthesis and their use as a compatibilizer in thiophene–quinoline polymer blends. *Macromolecules* **40**, 921–927 (2007).
20. B. Gholamkhass and S. Holdcroft: Toward stabilization of domains in polymer bulk heterojunction films. *Chem. Mater.* **22**, 5371–5376 (2010).
21. F. Goubard and G. Wantz: Ternary blends for polymer bulk heterojunction solar cells. *Polym. Int.* **63**, 1362–1367 (2014).
22. M.T. Dang, L. Hirsch, G. Wantz, and J.D. Wuest: Controlling the morphology and performance of bulk heterojunctions in solar cells. Lessons learned from the Benchmark poly(3-hexylthiophene): [6,6]-Phenyl-C61-butyric acid methyl ester system. *Chem. Rev.* **113**, 3734–3765 (2013).
23. K. Yuan, L. Chen, and Y. Chen: Nanostructuring compatibilizers of block copolymers for organic photovoltaics. *Polym. Int.* **63**, 593–606 (2014).
24. P.D. Topham, A.J. Parnell, and R.C. Hiorns: Block copolymer strategies for solar cell technology. *J. Polym. Sci. B: Polym. Phys.* **49**, 1131–1156 (2011).
25. G. Wantz, L. Derue, O. Dautel, A. Rivaton, P. Hudhomme, and C. Dagron-Lartigau: Stabilizing polymer-based bulk heterojunction solar cells via crosslinking. *Polym. Int.* **63**, 1346–1361 (2014).
26. B.J. Kim, Y. Miyamoto, B. Ma, and J.M.J. Frechet: Photocrosslinkable polythiophenes for efficient, thermally stable, organic photovoltaics. *Adv. Funct. Mater.* **19**, 2273–2281 (2009).
27. H.J. Kim, A-R. Han, C.-H. Cho, H. Kang, H.-H. Cho, M.Y. Lee, J.M.J. Fréchet, J.H. Oh, and B.J. Kim: Solvent-resistant organic transistors and thermally stable organic photovoltaics based on cross-linkable conjugated polymers. *Chem. Mater.* **24**, 215–221 (2012).
28. S. Khiev, L. Derue, G. Ayenew, H. Medlej, R. Brown, L. Rubatat, R.C. Hiorns, G. Wantz, and C. Dagron-Lartigau: enhanced thermal stability of organic solar cells by using photolinkable end-capped polythiophenes. *Polym. Chem.* **4**, 4145–4150 (2013).
29. M. Jeffries-El, G. Sauve, and R.D. McCullough: Facile synthesis of end-functionalized regioregular poly(3-alkylthiophene)s via modified grignard metathesis reaction. *Macromolecules* **38**, 10346–10352 (2005).
30. A. Yassara, L. Miozzoa, R. Girondaa, and G. Horowitz: Rod–coil and all-conjugated block copolymers for photovoltaic applications. *Prog. Polym. Sci.* **38**, 791–844 (2013).
31. M. Urien, H. Erothu, E. Cloutet, R.C. Hiorns, L. Vignau, and H. Cramail: Poly(3-hexylthiophene) based block copolymers prepared by "click" chemistry. *Macromolecules* **41**, 7033–7040 (2008).
32. Y. Tao, B. McCulloch, S. Kim, and R.A. Segalman: The relationship between morphology and performance of donor–acceptor rod–coil block copolymer solar cells. *Soft Matter* **5**, 4219–4230 (2009).
33. C.R. Craley, R. Zhang, T. Kowalewski, R.D. McCullough, and M.C. Stefan: Regioregular poly(3-hexylthiophene) in a novel conducting amphiphilic block copolymer. *Macromol. Rapid Commun.* **30**, 11–16 (2009).
34. S.-J. Mougnier, C. Brochon, E. Cloutet, G. Fleury, H. Cramail, and G. Hadziioannou: Design of well-defi ned monofunctionalized poly(3-hexylthiophene)s: toward the synthesis of semiconducting graft copolymers. *Macromol. Rapid Commun.* **33**, 703–709 (2012).
35. Z. Li, R.J. Ono, Z.-Q. Wu, and C.W. Bielawski: Synthesis and self-assembly of poly(3-hexylthiophene)-*block*-poly(acrylic acid). *Chem. Commun.* **47**, 197–199 (2011).
36. H. Erothu, J. Kolomanska, P. Johnston, S. Schumann, D. Deribew, D.T.W. Toolan, A. Gregori, C. Dagron-Lartigau, G. Portale, W. Bras, T. Arnold, A. Distler, R.C. Hiorns, P. Mokarian-Tabari, T.W. Collins, J.R. Howse, and P.D. Topham: Synthesis, thermal processing, and thin film morphology of poly(3-hexylthiophene)–poly(styrenesulfonate) block copolymers. *Macromolecules* **48**, 2107–2117 (2015).
37. R.H. Lohwasser and M. Thelakkat: Synthesis of amphiphilic rod–coil P3HT-b-P4VP carrying a long conjugated block using NMRP and click chemistry. *Macromolecules* **45**, 3070–3077 (2012).
38. H. Erothu, A.A. Sohdi, A.C. Kumar, A.J. Sutherland, C. Dagron-Lartigau, A. Allal, R.C. Hiorns, and P.D. Topham: Facile synthesis of poly (3-hexylthiophene)-blockpoly(ethylene oxide) copolymers via Steglich esterification. *Polym. Chem.* **4**, 3652–3655 (2013).
39. M. Jeffries-El, G. Sauvé, and R.D. McCullough: In-situ end-group functionalization of regioregular poly(3-alkylthiophene) using the grignard metathesis polymerization method. *Adv. Mater.* **16**, 1017–1019 (2004).
40. S. Kakogianni, S.N. Kourkouli, A.K. Andreopoulou, and J.K. Kallitsis: A versatile approach for creating hybrid semiconducting polymer–fullerene architectures for organic electronics. *J. Mater. Chem. A* **2**, 8110–8117 (2014).
41. J. Chen and Y. Cao: Development of novel conjugated donor polymers for high-efficiency bulk-heterojunction photovoltaic devices. *Acc. Chem. Res.* **42**, 1709–1718 (2009).
42. Y.J. Cheng, S.H. Yang, and C.S. Hsu: Synthesis of conjugated polymers for organic solar cell applications. *Chem. Rev.* **109**, 5868–5923 (2009).
43. M.-H. Yoon, C. Kim, A. Facchetti, and T.J. Marks: Gate dielectric chemical structure–organic field-effect transistor performance correlations for electron, hole, and ambipolar organic semiconductors. *J. Am. Chem. Soc.* **128**, 12851–12869 (2006).
44. D.J. Crouch, P.J. Skabara, J.E. Lohr, J.J.W. McDouall, M. Heeney, I. McCulloch, D. Sparrowe, M. Shkunov, S.J. Coles, P.N. Horton, and M.B. Hursthouse: Thiophene and selenophene copolymers incorporating fluorinated phenylene units in the main chain: synthesis, characterization, and application in organic field-effect transistors. *Chem. Mater.* **17**, 6567–6578 (2005).
45. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, and L. Yu: For the bright future—bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%. *Adv. Mater.* **22**, E135–E138 (2010).
46. P. Sonar, J. Chang, Z. Shi, J. Wu, and J. Li: Thiophene–tetrafluorophenyl–thiophene: a promising building block for ambipolar organic field effect transistors. *J. Mater. Chem. C* **3**, 2080–2085 (2015).
47. J.M. Lobez, T.L. Andrew, V. Buloviand, and T.M. Swager: Improving the performance of P3HT-fullerene solar cells with side-chain-functionalized poly(thiophene) additives: a new paradigm for polymer design. *ACS Nano* **6**, 3044–3056 (2012).
48. P. Giannopoulos, A. Nikolakopoulou, A.K. Andreopoulou, L. Sygellou, J. K. Kallitsis, and P. Lianos: An alternative methodology for anchoring organic sensitizers onto TiO_2 semiconductors for photoelectrochemical applications. *J. Mater. Chem. A* **2**, 20748–20759 (2014).
49. P. Giannopoulos, C. Anastasopoulos, A.K. Andreopoulou, and J. K. Kallitsis: Low-band gap electron-donor oligomeric sensitizers directly connected onto TiO2 nanoparticles for dye sensitized solar cells applications. *J. Surf. Interface Mater.* **2**, 274–279 (2014).
50. J. Liu, T. Tanaka, K. Sivula, A.P. Alivisatos, and J.M.J. Frechet: Employing end-functional polythiophene to control the morphology of nanocrystal–polymer composites in hybrid solar cells. *J. Am. Chem. Soc.* **126**, 6550–6551 (2004).
51. T. Rath and G. Trimme: In situ syntheses of semiconducting nanoparticles in conjugated polymer matrices and their application in photovoltaics. *Hybrid Mater.* **1**, 15–36 (2013).
52. J.N. Freitas, A.S. Gonçalves, and A.F. Nogueiras: A comprehensive review of the application of chalcogenide nanoparticles in polymer solar cells. *Nanoscale* **6**, 6371–6397 (2014).
53. Z.-S. Guo, L. Zhao, J. Pei, Z.-L. Zhou, G. Gibson, J. Brug, S. Lam, and S. S. Mao: CdSe/ZnS nanoparticle composites with amine-functionalized polyfluorene derivatives for polymeric light-emitting diodes: synthesis, photophysical properties, and the electroluminescent performance. *Macromolecules* **43**, 1860–1866 (2010).
54. H. Skaff, K. Sill, and T. Emrick: Quantum dots tailored with poly(paraphenylene vinylene). *J. Am. Chem. Soc.* **126**, 11322–11325 (2004).
55. T. de Roo, J. Haase, J. Keller, C. Hinz, M. Schmid, D.V. Seletskiy, H. Cölfen, A. Leitenstorfer, and S. Mecking: A direct approach to organic/

https://doi.org/10.1557/mrc.2015.42 Published online by Cambridge University Press

inorganic semiconductor hybrid particles via functionalized polyfluorene ligands. *Adv. Funct. Mater.* **24**, 2714–2719 (2014).
56. F. Monnaie, W. Brullot, T. Verbiest, J. De Winter, P. Gerbaux, A. Smeets, and G. Koeckelberghs: Synthesis of end-group functionalized P3HT: general protocol for P3HT/nanoparticle hybrids. *Macromolecules* **46**, 8500–8508 (2013).
57. A. Bousqueta, H. Awada, R.C. Hiorns, C. Dagron-Lartigau, and L. Billona: Conjugated-polymer grafting on inorganic and organicsubstrates: a new trend in organic electronic materials. *Prog. Polym. Sci.* **39**, 1847–1877 (2014).
58. L. Martinez, S. Higuchi, A.J. MacLachlan, A. Stavrinadis, N.C. Miller, S. L. Diedenhofen, M. Bernechea, S. Sweetnam, J. Nelson, S.A. Haque, K. Tajimaef, and G. Konstantatos: Improved electronic coupling in hybrid organic–inorganic nanocomposites employing thiol-functionalized P3HT and bismuth sulfide nanocrystals. *Nanoscale* **6**, 10018–10026 (2014).
59. S.M. Lindner and M. Thelakkat: Nanostructures of n-type organic semiconductor in a p-type matrix via self-assembly of block copolymers. *Macromolecules* **37**, 8832–8835 (2004).
60. S.M. Lindner, S. Huttner, A. Chiche, M. Thelakkat, and G. Krausch: Charge separation at self-assembled nanostructured bulk interface in block copolymers. *Angew. Chem., Int. Ed.* **45**, 3364–3368 (2006).
61. M. Sommer, S.M. Lindner, and M. Thelakkat: Microphase-separated donor–acceptor diblock copolymers: influence of homo energy levels and morphology on polymer solar cells. *Adv. Funct. Mater.* **17**, 1493–1500 (2007).
62. M. Sommer, A.S. Lang, and M. Thelakkat: Crystalline–crystalline donor–acceptor block copolymers. *Angew. Chem., Int. Ed.* **47**, 7901–7904 (2008).
63. Q.L. Zhang, A. Cirpan, T.P. Russell, and T. Emrick: Donor–acceptor poly (thiophene-*block*-perylene diimide) copolymers: synthesis and solar cell fabrication. *Macromolecules* **42**, 1079–1082 (2009).
64. S. Rajaram, P.B. Armstrong, B.J. Kim, and J.M.J. Frechet: Effect of addition of a diblock copolymer on blend morphology and performance of poly(3-hexylthiophene):perylene diimide solar cells. *Chem. Mater.* **21**, 1775–1777 (2009).
65. P. Mansky, Y. Liu, E. Huang, T.P. Russell, and C. Hawker: Controlling polymer-surface interactions with random copolymer brushes. *Science* **275**, 1458–1460 (1997).
66. B. Zhao and W. Brittain: Polymer brushes: surface-immobilized macromolecules. *Prog. Polym. Sci.* **25**, 677–710 (2000).
67. S. Campidelli, C. Sooambar, E.L. Diz, C. Ehli, D.M. Guldi, and M. Prato: Dendrimer-functionalized single-wall carbon nanotubes: synthesis, characterization, and photoinduced electron transfer. *J. Am. Chem. Soc.* **128**, 12544–12552 (2006).
68. C. Cioffi, S. Campidelli, C. Sooambar, M. Marcaccio, G. Marcolongo, M. Meneghetti, D. Paolucci, F. Paolucci, C. Ehli, G.M.A. Rahman, V. Sgobba, D.M. Guldi, and M. Prato: Synthesis, characterization, and photoinduced electron transfer in functionalized single wall carbon nanohorns. *J. Am. Chem. Soc.* **129**, 3938–3945 (2007).
69. N. Karousis, N. Tagmatarchis, and D. Tasis: Current progress on the chemical modification of carbon nanotubes. *Chem. Rev.* **110**, 5366–5397 (2010).
70. D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato: Chemistry of carbon nanotubes. *Chem. Rev.* **106**, 1105–1136 (2006).
71. A.A. Stefopoulos, C.L. Chochos, M. Prato, G. Pistolis, K. Papagelis, F. Petraki, S. Kennou, and J.K. Kallitsis: Novel hybrid materials consisting of regioregular poly(3-octylthiophene)s covalently attached to single-wall carbon nanotubes. *Chem. Eur. J.* **14**, 8715–8724 (2008).
72. C.L. Chochos, A.A. Stefopoulos, S. Campidelli, M. Prato, V.G. Gregoriou, and J.K. Kallitsis: Immobilization of oligoquinoline chains on single-wall carbon nanotubes and their optical behavior. *Macromolecules* **41**, 1825–1830 (2008).
73. A.A. Stefopoulos, S.N. Kourkouli, S. Economopoulos, F. Ravani, A. Andreopoulou, K. Papagelis, A. Siokou, and J.K. Kallitsis: Polymer and hybrid electron accepting materials based on a semiconducting perfluorophenylquinoline. *Macromolecules* **43**, 4827–4828 (2010).
74. S.N. Kourkouli, A. Siokou, A.A. Stefopoulos, F. Ravani, T. Plocke, M. Müller, J. Maultzsch, C. Thomsen, K. Papagelis, and J.K. Kallitsis: Electronic properties of semiconducting polymer-functionalized single wall carbon nanotubes. *Macromolecules* **46**, 2590–2598 (2013).
75. B. de Boer, U. Stalmach, P.F. van Hutten, C. Melzer, V.V. Krasnikov, and G. Hadziioannou: Supramolecular self-assembly and opto-electronic properties of semiconducting block copolymers. *Polymer* **42**, 9097–9109 (2001).
76. M.H. van der Veen, B. de Boer, U. Stalmach, K.I. van de Wetering, and G. Hadziioannou: Donor–acceptor diblock copolymers based on PPV and C60: synthesis, thermal properties, and morphology. *Macromolecules* **37**, 3673–3684 (2004).
77. S. Barrau, T. Heiser, F. Richard, C. Brochon, C. Ngov, K. van de Wetering, G. Hadziioannou, D.V. Anokhin, and D. Ivanov: A. Self-assembling of novel fullerene-grafted donor–acceptor rod–coil block copolymers. *Macromolecules* **41**, 2701–2710 (2008).
78. K. Sivula, Z.T. Ball, N. Watanabe, and J.M.J. Frechet: Amphiphilic diblock copolymer compatibilizers and their effect on the morphology and performance of polythiophene:fullerene solar cells. *Adv. Mater.* **18**, 206–210 (2006).
79. F. Richard, C. Brochon, N. Leclerc, D. Eckhardt, T. Heiser, and G. Hadziioannou: Design of a linear poly(3-hexylthiophene)/fullerene-based donor–acceptor rod–coil block copolymer. *Macromol. Rapid. Commun.* **29**, 885–891 (2008).
80. M. Li, P. Xu, J. Yang, and S. Yang: Donor-π-acceptor double-cable polythiophenes bearing fullerene pendant with tunable donor/acceptor ratio: a facile postpolymerization. *J. Mater. Chem.* **20**, 3953–3960 (2010).
81. M. Dante, C. Yang, B. Walker, F. Wudl, and T.-Q. Nguyen: Self-assembly and charge-transport properties of a polythiophene–fullerene triblock copolymer. *Adv. Mater.* **22**, 1835–1839 (2010).
82. R.C. Hiorns, P. Iratçabal, D. Be´gue´, A. Khoukh, R. De Bettignies, J. Leroy, M. Firon, C. Sentein, H. Martinez, H. Preud'homme, and C. Dagron-Lartigau: Alternatively linking fullerene and conjugated polymers. *J. Polym. Sci. A: Polym. Chem.* **47**, 2304–2317 (2009).
83. J.U. Lee, J.W. Jung, T. Emrick, T.P. Russell, and W.H. Jo: Synthesis of C60-end capped P3HT and its application for high performance of P3HT/PCBM bulk heterojunction solar cells. *J. Mater. Chem.* **20**, 3287–3294 (2010).
84. B. Gholamkhass, T.J. Peckham, and S. Holdcroft: Poly (3-hexylthiophene) bearing pendant fullerenes: aggregation vs. self-organization. *Polym. Chem.* **1**, 708–719 (2010).
85. J.U. Lee, A. Cirpan, T. Emrick, T.P. Russell, and W.H. Jo: Synthesis and photophysical property of well-defined donor–acceptor diblock copolymer based on regioregular poly(3-hexylthiophene) and fullerene. *J. Mater. Chem.* **19**, 1483–1489 (2009).
86. C. Yang, J.K. Lee, A.J. Heeger, and F. Wudl: Well-defined donor–acceptor rod–coil diblock copolymers based on P3HT containing C60: the morphology and role as a surfactant in bulk-heterojunction solar cells. *J. Mater. Chem.* **19**, 5416–5423 (2009).
87. E. Bicciocchi, M. Chen, E. Rizzardo, and K.P. Ghiggino: Synthesis of a rod–coil block copolymer incorporating PCBM. *Polym. Chem.* **4**, 53–56 (2013).
88. M. Chen, M. Li, H. Wang, S. Qu, X. Zhao, L. Xie, and S. Yang: Side-chain substitution of poly(3-hexylthiophene) (P3HT) by PCBM via postpolymerization: an intramolecular hybrid of donor and acceptor. *Polym. Chem.* **4**, 550–557 (2013).
89. N. Sary, F. Richard, C. Brochon, N. Leclerc, P. Lévêque, J.-N. Audinot, S. Berson, T. Heiser, G. Hadziioannou, and R. Mezzenga: A new supramolecular route for using rod–coil block copolymers in photovoltaic applications. *Adv. Mater.* **22**, 763–768 (2010).
90. C. Renaud, S.-J. Mougnier, E. Pavlopoulou, C. Brochon, G. Fleury, D. Deribew, G. Portale, E. Cloutet, S. Chambon, L. Vignau, and G. Hadziioannou: Block copolymer as a nanostructuring agent for high efficiency and annealing-free bulk heterojunction organic solar cells. *Adv. Mater.* **24**, 2196–2201 (2012).
91. A. Laiho, R.H.A. Ras, S. Valkama, J. Ruokolainen, R. Österbacka, and O. Ikkala: Control of self-assembly by charge-transfer complexation between c60 fullerene and electron donating units of block copolymers. *Macromolecules* **39**, 7648–7653 (2006).
92. M. Wang, A.J. Heeger, and F. Wudl: Self-assembly of a fullerene poly (3-hexylthiophene) dyad. *Small* **7**, 298–301 (2011).

https://doi.org/10.1557/mrc.2015.42 Published online by Cambridge University Press

93. D.A. Kamkar, M. Wang, F. Wudl, and N. Thuc-Quyen: Single nanowire OPV properties of a fullerene-capped P3HT dyad investigated using conductive and photoconductive AFM. *ACS Nano* **6**, 1149–1157 (2012).
94. M. Wang and F. Wudl: Top-down meets bottom-up: organized donor–acceptor heterojunctions for organic solar cells. *J. Mater. Chem.* **22**, 24297–24314 (2012).
95. M. Yan, S.X. Cai, and J.F.W. Keana: Photochemical and thermal reactions of C60 with N-succinimidyl 4-azido-2,3,5,6-tetrafluorobenzoate: a new method for functionalization of C60. *J. Org. Chem.* **59**, 5951–5954 (1994).
96. M. Cases, M. Duran, J. Mestres, N. Martín, and M. Solà: Mechanism of the addition reaction of alkyl azides to [60]fullerene and the subsequent N2 extrusion to form monoimino-[60]fullerenes. *J. Org. Chem.* **66**, 433–442 (2001).
97. S.J. Pastine, D. Okawa, B. Kessler, M. Rolandi, M. Llorente, A. Zettl, and J.M.J. Fréchet: A facile and patternable method for the surface modification of carbon nanotube forests using perfluoroarylazides. *J. Am. Chem. Soc.* **130**, 4238–4239 (2008).
98. K. Suggs, D. Reuven, and X.-Q. Wang: Electronic properties of cycloaddition-functionalized graphene. *J. Phys. Chem. C* **115**, 3313–3317 (2011).
99. L.-H. Liu and M. Yan: Perfluorophenyl azides: new applications in surface functionalization and nanomaterial synthesis. *Acc. Chem. Res.* **43**, 1434–1443 (2010).
100. B. Yameen, T. Puerckhauer, J. Ludwig, I. Ahmed, O. Altintas, L. Fruk, A. Colsmann, and C. Barner-Kowollik: π-conjugated polymer–fullerene covalent hybrids via ambient conditions diels–alder ligation. *Small* **10**, 3091–3098 (2014).
101. R.C. Hiorns, E. Cloutet, E. Ibarboure, A. Khoukh, H. Bejbouji, L. Vignau, and H. Cramail: Synthesis of donor-acceptor multiblock copolymers incorporating fullerene backbone repeat units. *Macromolecules* **43**, 6033–6044 (2010).
102. L. Perrin, M. Legros, and R. Mercier: Design of a series of polythiophenes containing C60 groups: synthesis and optical and electrochemical properties. *Macromolecules* **48**, 323–336 (2015).

https://doi.org/10.1557/mrc.2015.42 Published online by Cambridge University Press