JOURNAL OF
Materials
CHEMISTRY
Feature Article

Double-cable polymers for fullerene based organic optoelectronic applications

Antonio Cravino* and Niyazi Serdar Sariciftci

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, A-4040 Linz, Austria. E-mail: antonio.cravino@jku.at; Fax: +43-732-2468-8770; Tel: +43-732-2468-8767

Received 12th February 2002, Accepted 24th April 2002
First published as an Advance Article on the web 16th May 2002

Conjugated polymers are used increasingly for the fabrication of electronic and optoelectronic devices like light emitting diodes (LEDs) and photovoltaic (PV) elements. A breakthrough in realising a promisingly efficient conversion of solar energy into electrical energy has been achieved by using blends of soluble electron-donor type conjugated polymers with fullerenes as electron-acceptor, transporting component. This "bulk heterojunction" approach suggests the preparation of intrinsically bipolar materials as a way to control both electronic and morphological properties at once. On these bases, the covalent grafting of fullerene moieties to conjugated backbones seems promising for the preparation of intrinsically bipolar polymeric materials (*double-cable* polymers) alternative to conjugated polymer/ fullerene composites. The recent developments on the design, the characterisation and the application of this novel class of fullerene functional materials are reviewed.

1 Introduction

During the last twenty years, the attention of many researchers has been increasingly devoted to the synthesis and the understanding of molecules with extended, delocalised π-electron systems. In addition to the development of new exciting concepts, this work has opened a viable way to the use of organic materials like fullerenes[1–8] and conjugated polymers[9–12] in application fields traditionally reserved to inorganic semiconductors and metals. For instance, after a period of academic research, polymeric displays and LEDs are nowadays entering the display market.[13–16] Furthermore, since the discovery of a photoinduced electron transfer from non-degenerate ground-state conjugated polymers to fullerenes,[17,18] these materials are considered for the cost effective fabrication of flexible large-area solar cells and photodetectors.[19,20]

Organic solar cells of the first generation were *p*/*n*-heterojunction diodes, consisting of an electron-donor molecule (*p*-type component) thin film and an acceptor molecule (*n*-type component) thin film sandwiched between metal contacts. The flat heterojunction of two organic thin films gives rise to rectification behaviour as well as photocurrent and PV effects.[21–27] However, in this type of device, the effective interaction between the electron-donor and the electron-acceptor components is limited to the flat geometrical interface. As such, rather low short circuit photocurrent density (J_{SC}) values were obtained. A breakthrough has been achieved by direct mixing of a soluble *p*-type conjugated polymer and C_{60}, or other fullerene derivatives, as *n*-type component (Fig. 1).[27,28] Effective interaction between the donor and the acceptor components within these "bulk-heterojunction" solar cells can take place in the entire device's volume. Therefore, a more efficient charge generation results in dramatically enhanced short circuit J_{SC} values and in turn in much more efficient PV devices. However, the performance of "bulk-heterojunction" solar cells is still affected by critical factors:

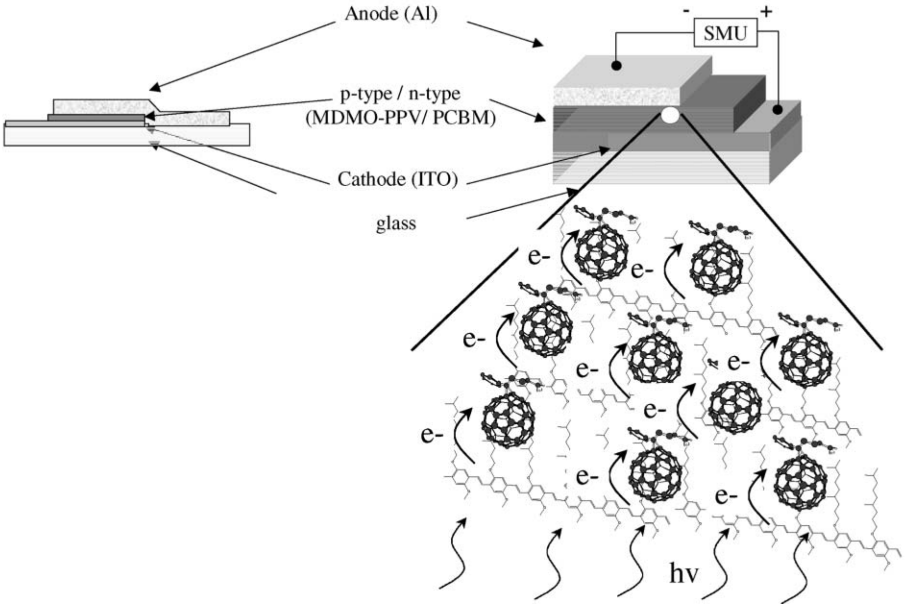


Fig. 1 Schematic representation of a "bulk-heterojunction" photovoltaic device. (Reproduced from ref. 27 with permission of WILEY-VCH.)

DOI: 10.1039/b201558g

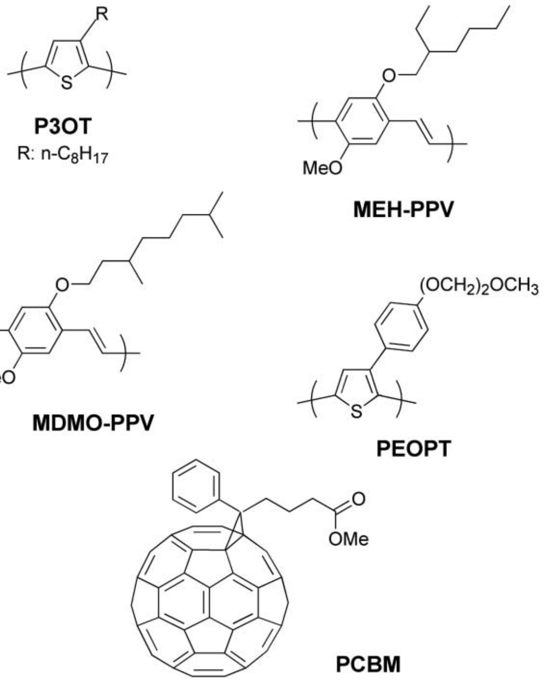


Chart 1

- The compatibility between the conjugated polymer and the fullerene components plays a crucial role in determining the final morphology of the blend. Phase separation and clustering of fullerene can occur, reducing the effective donor/acceptor interfacial area as compared to the ideal value.[29]
- Moreover, in this device architecture, a balanced transport of both photogenerated electrons and holes would be highly important. For an efficient transport of holes through the donor polymer matrix and of electrons through the acceptor fullerene phase, a truly bicontinuous interpenetrating network is required. Clustering effects, leading to a "void" between *p*- as well as *n*-type domains, obviously dramatically affect the transport of charges.[29]

Therefore, it is indeed intriguing to think of single materials with intrinsic donor–acceptor properties as well as the capability of both electron and hole transport (*p*/*n*-type material).

An elegant way towards such a target is offered by the design and the synthesis of *p*-type conjugated backbones (donor-*cable*) bearing directly grafted or tethered acceptor groups such as fullerene moieties (acceptor-*cable*). In this way, the secondary structure of the macromolecule might possibly be dictated by its primary structure (*double-cable* polymer). The effective donor/acceptor interfacial area will be maximised, and phase separation and clustering phenomena should be prevented as well. In addition, the interaction between the donor conjugated backbone and the acceptor moieties may be tuned by varying the chemical structure (nature and length) of their connecting fragment.[30] Basically, the realisation of effective *double-cable* polymers will bring the *p*/*n*-heterojunction at the molecular level. In this paper, after a brief description of the photophysical properties of conjugated polymer/fullerene composites and of the "bulk-heterojunction" solar cells fabricated using them, the recent progresses on the design, the characterisation and the preliminary application of *double-cables* consisting of a conjugated backbone bearing fullerene moieties are reviewed. Even though the search for other alternative electron accepting components to fullerenes has been pursued,[31–36] the results so far obtained indicate fullerenes to be specially interesting functional materials.[27,29,37,38]

2 Ultrafast photoinduced electron transfer from conjugated polymers onto fullerenes

Most of non-degenerate ground-state conjugated polymers in their photoexcited states (electrons promoted to the antibonding π^* band) are electron donors. The stability of quasi-particles on conjugated polymers (*e.g.* radical-ions such as polarons)[39,40] suggested their use in combination with electron acceptor molecules. In 1992, Sariciftci *et al.* and Morita *et al.* independently reported the spectroscopic and photophysical properties of blends composed of poly[(2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylene) vinylene] or poly(3-octylthiophene) (MEH-PPV and P3OT, respectively, see Chart) and C$_{60}$.[17,18] While no ground-state interaction between the two components was observed, a strong quenching of the MEH-PPV luminescence indicated the existence of a sub-picosecond photoinduced electron transfer.[41] The same behaviour was observed later in a number of conjugate polymer/fullerene composites. Very recently, the transfer of electrons from photoexcited conjugated polymers onto 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C$_{61}$ (PCBM, see Chart) has been studied by pump-probe measurements with the unprecedented time resolution of 10 fs.[42] The experimental set-up allowed to time-resolve the photoinduced electron transfer time with about 40 fs after an initial Kasha relaxation.[42] This high rate results in a very efficient electron transfer, with a quantum yield that approaches unity. Time-resolved photocurrent studies on MEH-PPV/C$_{60}$ composites with different C$_{60}$ percentage contents showed that the fullerene not only enhances the number of the charge carriers photogenerated in the host polymeric matrix, but also stabilises them preventing their recombination.[43] Finally, a direct and definitive evidence for an electron transfer from photoexcited conjugated polymers onto fullerenes, leading to long-lived charged states, was obtained by steady-state light induced electron spin resonance (LESR) experiments. As an example, Fig. 2 displays the integrated LESR signal recorded upon illumination of MDMO-PPV/PCBM composites (MDMO-PPV stands for poly[(2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-phenylene) vinylene], see Chart).[44,45] Two light induced electron spin resonance signals can be resolved: one at $g = 2.0026$, assigned to radical-cations (positive polarons) on the conjugated backbone and one at $g = 1.9997$, assigned to PCBM$^{\bullet -}$ radical-anions.[44,45]

The long-lived nature of the charge carriers photogenerated within conjugated polymer/fullerene composites allows their collection at electrodes *via* diffusion as well as field induced migration and their use to provide electrical power to an external circuit. As such, these materials are rather attractive for PV solar energy conversion, and have been used for the fabrication of plastic solar cells as described in the next section.

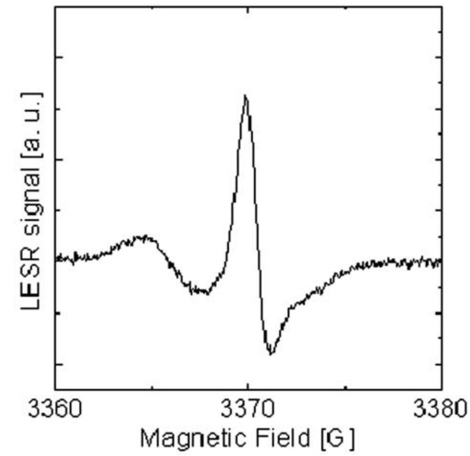


Fig. 2 Integrated LESR spectrum of a MDMO-PPV/PCBM composite upon successive illumination with 2.41 eV argon ion laser. (Reproduced from ref. 45 with the permission of the American Physical Society.)

3 "Bulk-heterojunction" plastic solar cells

In this section, we introduce plastic solar cells based on the "bulk-heterojunction" approach with the aim of elucidating the relationship between the morphology of the photoactive layer and the device's performance. Ref. 27 gives a general and updated overview on organic, plastic PV. A discussion on the working principle of conjugated polymer/fullerene "bulk-heterojunction" solar cells, and specifically on the origin of their open circuit voltage (V_{OC}), can be found in refs. 37 and 46.

Extensive literature exists on the realisation of bilayer photovoltaic elements based on small organic molecules, conjugated polymers and fullerene.[21–26,47,48] Although, as mentioned above, the internal quantum efficiency of photo-induced charge separation is approaching unity for a donor–acceptor pair, the power conversion efficiency of these devices is limited by interconnected factors:

- charge separation occurs only at the flat geometrical interface, within the exciton diffusion length. Photoexcitations created far away from the heterojunction undergo recombination prior to reaching the electrodes;
- only a small fraction of incident photons is absorbed near the heterojunction interface.

To overcome these problems, "bulk-heterojunction" solar cells, whose photoactive layer consists of a conjugated polymer/fullerene blend, have been designed.[27,28] The cross-section of this type of device as well as the distribution of the conjugated polymer chains and fullerene molecules within the "bulk-heterojunction" are sketched schematically in Fig. 1.

Besides small-area testing devices, technologically more interesting scaled-up large-area (15 cm × 10 cm) PV elements on flexible plastic substrates were produced as well.[27] A large-area solar cell is shown in Fig. 3 while its current voltage (*I*/*V*) characteristics are plotted in Fig. 4. For these devices the "bulk-heterojunction" approach introduced above was used, by mixing MDMO-PPV and PCBM (Fig. 1).[27] The comparison of these devices with the small-area solar cells on rigid substrate clearly showed that scaling-up to large-area flexible devices is possible, giving routinely efficiencies as high as 2.5% under AM1.5 illumination.

3.1 Improving the efficiency of "bulk-heterojunction" solar cells

Recently, it has been demonstrated that the efficiency of "bulk-heterojunction" plastic solar cells can be improved by manipulating the *morphology* within the photoactive blend.[29]

Fig. 3 Picture of a large area flexible plastic solar cell. (Reproduced with permission of WILEY-VCH.)

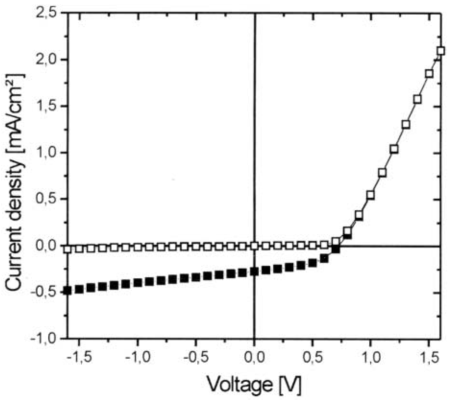


Fig. 4 I/V behaviour of a 15 cm × 10 cm MDMO-PPV/PCBM "bulk-heterojunction" solar cell, with active area of 50 cm^2 under light (black squares) and in the dark (open squares). Illumination was provided by a white-light fluorescence tube with intensity of 6 mW cm^{-2}. (Reproduced from ref. 27 with permission of WILEY-VCH.)

The sketch given by Fig. 1 is by far not realistic in any actual composite. Composites are indeed juxtapositions of domains with different composition. Fig. 5 shows images of the surfaces of MDMO-PPV/PCBM blends spin-coated from toluene solution (a) and chlorobenzene solutions (b), respectively, obtained by atomic force microscopy (AFM). The images show that a more homogenous mixing of the two components is obtained when chlorobenzene is used as processing solvent. Very recent morphological studies, done by comparing AFM surface images and cross-sectional transmission electron microscopy (TEM) images, clearly confirm this observation.[49] The impact of these two highly different morphologies to the PV device performance was studied fabricating solar cells under identical conditions except for the choice of the solvent. The

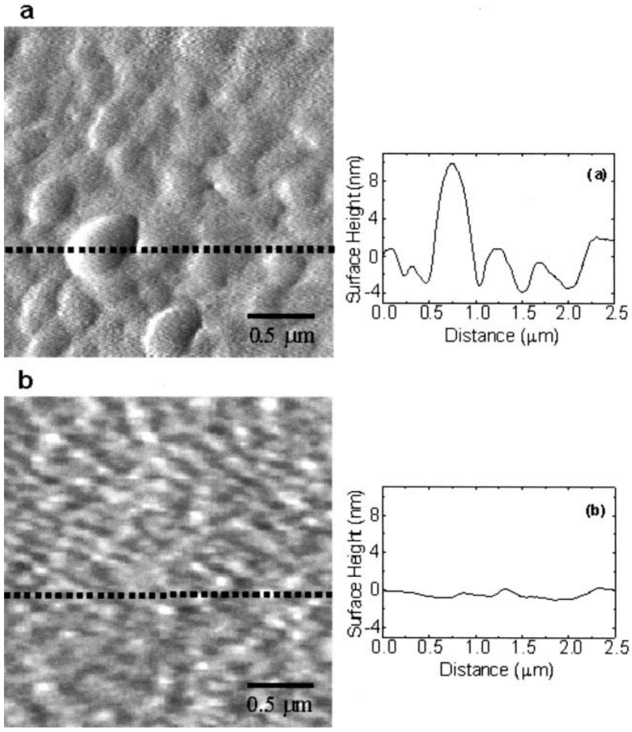


Fig. 5 AFM images showing the surface morphology of MDMO-PPV/PCBM (1 : 4 w/w) blend films with thickness of *ca.* 100 nm and the corresponding cross-section. **a)** Film spun-cast from solution in toluene. **b)** Film spun-cast from solution in chlorobenzene. The images show the first derivative of the actual surface heights. The cross sections of the true surface heights were taken horizontally from the points indicated by the dotted lines. (Reproduced from ref. 27 with permission of VILEY-VCH.)

open circuit photovoltages for the two types of devices are almost identical while the device cast from chlorobenzene solution exhibits more than a twofold enhancement in the J_{SC} as compared to the device fabricated from toluene solution (5.25 *versus* 2.33 mA cm^{-2}). This high J_{SC} value, combined with a fill factor (FF) as high as 0.61, results in a power efficiency η of 2.5% under AM1.5 illumination.[50] This is the highest efficiency so far reported for plastic solar cells. The optical absorption spectra of the active layer are nearly identical in the two cases, while the incident current to photon efficiency (IPCE, also called external quantum efficiency, EQE) of the device made from chlorobenzene is higher all over the absorption spectrum. As such, the difference in the device efficiencies must be related to the different morphologies shown by Fig. 5. Shrinking each of the interpenetrating two phases' domain size leads to a larger donor–acceptor interfacial area and decreases the spatial separation between fullerene domains. Indeed, the increase in efficiency relies also on the increased mobility of the charge carriers of both signs, as indicated by field-effect measurements on the single components as well as on the composite, spun-cast from different solvents.[51]

Different strategies to improve the processability of fullerenes and/or to achieve their intimate mixing with conjugated polymers have been proposed. To control the morphology within the photoactive layer and to obtain a predetermined nanoscopic phase-separated network, systems as diblock-copolymers (conjugated donor block plus fullerene-bearing block)[52] and conjugated oligomer–fullerene dyads have been prepared.[53–61] Peeters *et al.* used an oligo(*p*-phenylene vinylene)-fulleropyrrolidine dyad to fabricate solar cells with efficiencies comparable to those of other previously reported "bulk-heterojunction" solar cells.[60] However, for several donor–acceptor dyads it was found that depending on a number of factors (*e.g.* environment, conjugation length of the donor unit, *etc.*) photoinduced energy transfer can compete with photoinduced electron transfer.[59–62] Conjugated oligomer–fullerene dyads, containing donor moieties with different conjugation lengths, have also been tested as embedded components in a MDMO-PPV matrix. By comparing the performance of the obtained PV devices, it seems that dyads capable of intramolecular electron transfer (those with longer conjugated oligomer moieties) also enhance geminate carrier recombination.[63,64] This appears plausible, since on dyads separated charges can escape recombination only by intermolecular hopping. On the contrary, in system with a long conjugated donor backbone bearing a number of acceptor fullerene moieties—such as *double-cable* polymers—it can be expected that holes migrate away from electrons by a very fast intrachain diffusion process, preventing recombination. Therefore, *double-cable* polymers appear very interesting as materials that may retain the favourable electronic and photophysical properties of conjugated polymer/fullerene composites but in which phase separation and clustering phenomena cannot occur.

4 Towards "molecular heterojunction": the donor–acceptor *double-cable* polymers

A "bulk-heterojunction" (a) (where the occurrence of fullerene clustering is emphasized for clarity), an ordered ideal *double-cable* polymer chain (b), and a picture in which the continuous pathway for the transport of electrons is given by the contacts between fullerene moieties on different polymer chains (c) are schematically depicted in Fig. 6. Besides other aspects like the relative positioning of the polymer chain and the fullerene moieties, as well as the positioning of a fullerene moiety with respect to its neighbours (and chain to chain), a *double-cable* polymer for PV application must meet the following requirements:

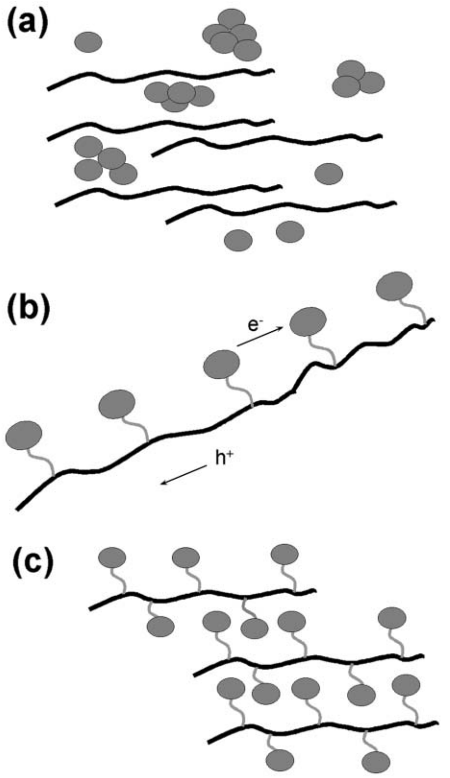
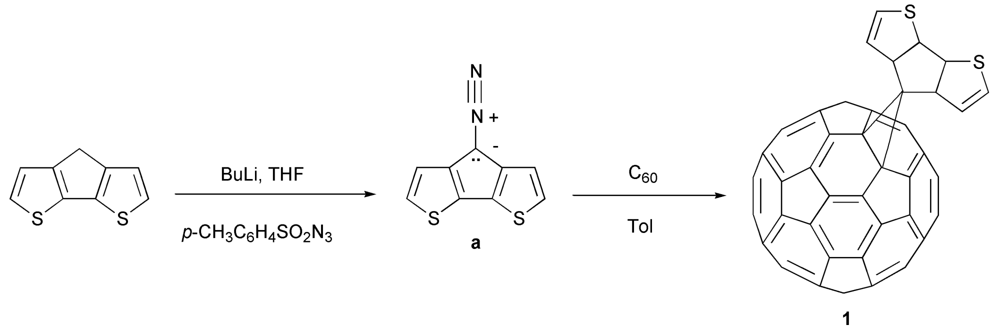


Fig. 6 **a)** Schematic representation of a "bulk-heterojunction". Clustering of the fullerene component is emphasised. **b)** An ideal, ordered *double-cable* polymer and **c)** a more realistic picture where interchain interactions are considered.

- mutually independent ground-state electronic properties of the donor backbone and of the fullerene acceptor moieties ("the cables must not short");
- a photoinduced electron transfer from the electron-donating backbone onto the electron-accepting fullerene moiety, leading to metastable long-lived charged states, as a prerequisite for photogeneration of free charge carriers.

In addition, solubility in common organic solvents is also a determinant factor, since the easy and cost-effective preparation of thin film devices involves processing from solutions.

A route towards the preparation of conjugated polymers is electropolymerisation of suitable aromatic monomers. Electropolymerisation generally proceeds *via* electrogeneration of radical-cations as reactive species and their subsequent coupling followed by rearomatisation steps.[65,66] Several attempts at the preparation of novel and exotic conjugated polymers, some of them carrying electroactive moieties,[67] have been made synthesising molecules specifically designed as substrates for electropolymerisation.[66] Moreover, electropolymerisation allows the growth of polymeric thin films onto transparent electrodes suitable for most spectroscopic techniques. This is a clear advantage when solubility of a novel conjugated polymer cannot be obtained. As already mentioned, it has been observed that in molecular donor–acceptor dyads photoinduced energy transfer can take place competing with intramolecular charge transfer, and geminate recombination may also be enhanced. Similar effects could occur even in *double-cable* polymers. Therefore, for the design of polymers and supramolecular structures for photovoltaic materials,[68] the electrochemical approach has been selected as a first step towards *double-cable* polymers as well as for the study of their electronic and photophysical behaviour. However, as explained above, solubility is a desired requirement for practical applications. Based on the positive results obtained with insoluble electropolymerised *double-cable* polymers, the chemical preparation of soluble *double-cables* is proceeding worldwide.

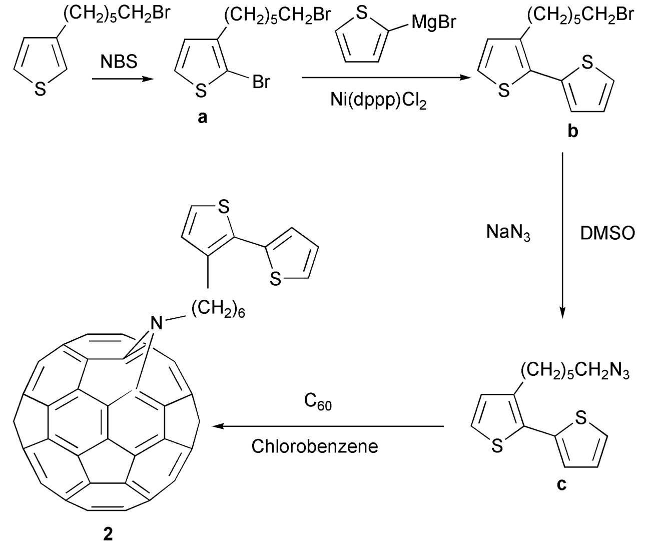


Scheme 1

4.1 Electropolymerised *double-cable* polymers.

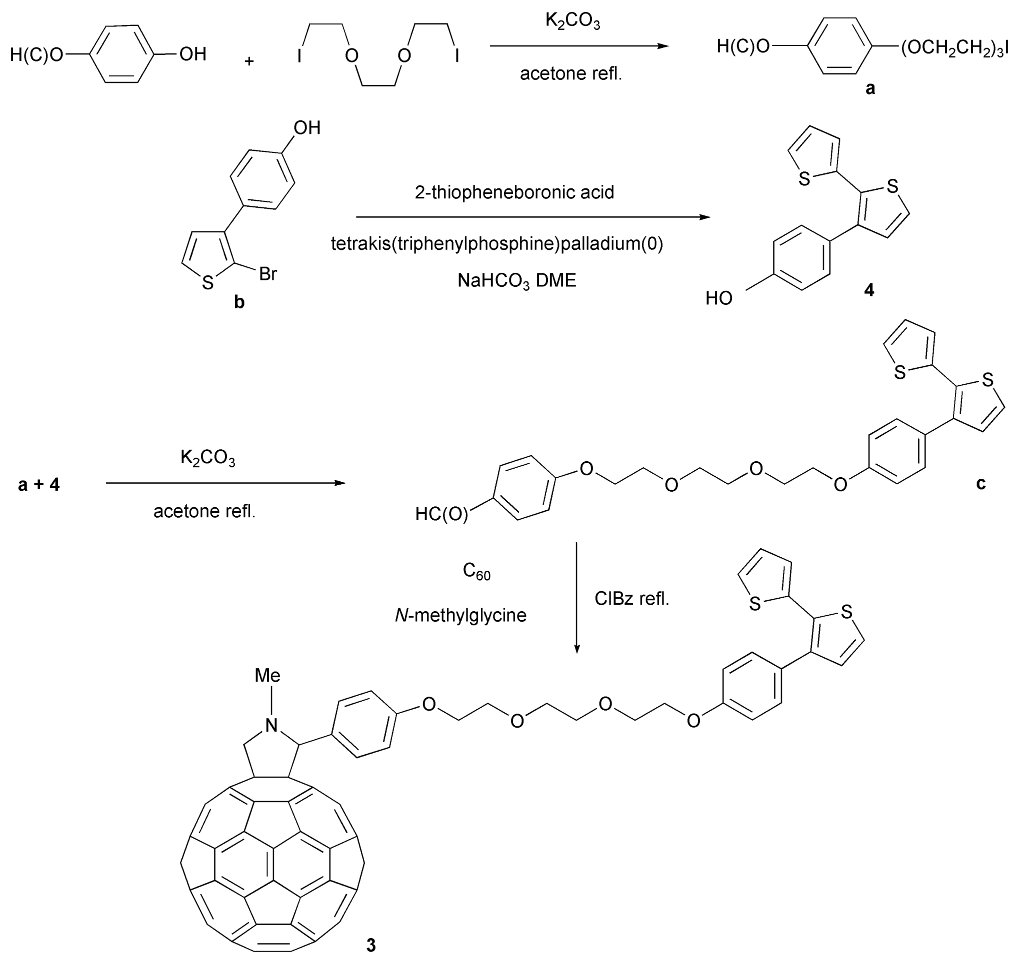
The first conjugated polymeric material bearing fullerene side groups was reported in 1996 by Benincori *et al.*[69] They described the direct grafting of C_{60} at the bridging carbon of cyclopentadithiophene (Scheme 1), leading to compound **1** which was suitable for electropolymerisation. The stable cyclopentadithiophene diazo-derivative **a** was obtained by "diazo-group transfer". Its treatment with one equivalent of C_{60} in toluene solution at room temperature for 12 h gave **1**. Due to its low solubility in mixtures containing acetonitrile, the anodic electropolymerisation of **1** was possible only in chlorobenzene. After dedoping, poly-**1** showed an absorption spectrum with maximum at $\lambda = 440$ nm (onset above 600 nm). This $\lambda_{\max}$ value, which is considerably blue-shifted (about 100 nm) as compared to that of electropolymerised unsubstituted cyclopentadithiophene, was explained as consequence of the poor solubility mentioned above, leading to relatively short chains (and, therefore, to a short effective conjugation length). The electrochemical behaviour of poly-**1** films was studied by cyclic voltammetry in monomer-free conditions. One anodic reversible wave corresponding to the electrochemical oxidation/rereduction (*p*-doping/dedoping) of the polyconjugated chain was observed at a potential 0.55 V more positive than that of the corresponding process in polycyclopentadithiophene. This result was explained as due to the electron withdrawing effect of the fullerene moieties. By scanning negative potential, three reversible waves, assigned to the multiple fullerene substituent reduction/reoxidation steps,[70] were observed.

One year later, Ferraris *et al.* reported the synthesis (Scheme 2) and the electrochemical polymerisation of a bithiophene carrying a fullerene group through a flexible alkyl chain spacer (**2**).[71,72] The choice of **2** was motivated by the lower oxidation potential of bithiophenes as compared to thiophenes, generally leading to easier and superior electropolymerisability.[65,66] Moreover, the flexible alkyl spacer was introduced to impart solubility to the monomer as well as to reduce the electron withdrawing effect of the fullerene moiety. Monomer **2** was prepared as follows (Scheme 2): 2-bromo-3-(6-bromohexyl)thiophene (**a**) was obtained by bromination of 3-(6-bromohexyl)thiophene with NBS in chloroform–acetic acid solution. 3′-(6-Bromohexyl)-2,2′-bithienyl (**b**) was prepared by coupling the Grignard's reagent obtained from 2-bromothiophene and 2-bromo-3-(6-bromohexyl)thiophene. The reaction of the bithienyl derivative **b** with sodium azide in DMSO afforded the desired azide **c** in quantitative yield. Treatment of **c** with C_{60} in refluxing chlorobenzene gave the monoadduct **2**, which was purified by column chromatography. In contrast to C_{60} and **1**, monomer **2** was indeed soluble in several organic solvents like chloroform, dichloromethane and THF. These improved characteristics resulted in an electropolymerised material that showed, in its neutral state, an absorption maximum at $\lambda = 480$ nm. This value is comparable to that of most polythiophenes, indicating almost no electronic or steric perturbation of the conjugated chain. Similarly, electrochemical and *in situ* UV-Vis spectroelectrochemical measurements revealed that the polymeric chain in poly-**2** behaves as common polythiophenes do. In the cathodic region of the cyclic voltammogram (CV) of poly-**2**, four fullerene reduction/reoxidation waves were observed.[70] These results indicated that in *double-cable* polymers both the donor polyconjugated chain and the fullerene acceptor moieties can retain, with different extents, their individual electronic and electrochemical properties. In particular, by using flexible spacers of the proper length, the donor and acceptor moieties can be electronically "isolated" in order to prevent ground-state interactions. As such, these early works already showed that *double-cable* polymers could meet the first requirement for PV applications.



Scheme 2

Polythiophene P3OT in combination with C_{60} or PCBM has been also used for fabricating promising "bulk-heterojunction" solar cells,[73,74] suggesting polythiophene-fullerene based *double-cables* for further studies on PV applications. The preparation of bithiophene–fulleropyrrolidine dyad **3** was reported recently (Scheme 3).[75,76] Reaction between commercially available 4-hydroxybenzaldehyde and 2-[2-(iodoethoxy)ethoxy]ethane in the presence of K_2CO_3 in refluxing acetone afforded the monosubstituted product **a** in 20% yield. Palladium-catalysed coupling of 4-bromophenol with 3-thiopheneboronic acid followed by bromination with NBS gave the reactive 2-bromo-3-(*p*-hydroxyphenyl)thiophene **b** that was coupled directly with 2-thiopheneboronic acid to afford the desired bis-thiophene phenol **4**. Reaction of **a** with the potassium salt of bis-thiophene phenol **4** gave the functionalised bithiophene **d** used for the Prato's reaction to obtain **3** in 49% isolated yield. According to the criteria already exploited by Ferraris *et al.*,[66,72] bithiophene **3** was found appropriate for relatively facile anodic electropolymerisation. Both dichloromethane and



Scheme 3

toluene–acetonitrile mixtures were suitable as solvents. As a major result, the obtained poly-**3** films allowed the first observation of a photoinduced electron transfer from the polythiophene backbone to the pendant fullerene moieties within a *double-cable* polymer, as discussed in the following.

The cyclic voltammogram of **3**, recorded during potential cycling between 0 and 1.6 V, (Ag/AgCl wire as quasi-reference electrode, −0.44 V *vs.* ferrocene) is illustrated in Fig. 7 (Pt as working electrode). The first scan shows one irreversible wave peaking at *ca.* +1.3 V, corresponding to the oxidation of **3**. Recurrent potential scanning leads to the development of a new redox wave around +0.8 V, related to the *p*-doping/dedoping of a freshly formed poly-**3** film. Analogous results were obtained using different solvents (toluene–acetonitrile mixtures) and ITO coated transparent electrodes. Poly-**4** was also prepared as a reference material following the same electrochemical procedure.[38,75] The CV of a poly-**3** film in monomer-free electrolyte solution is depicted in Fig. 8(a). In the positive region, one reversible redox process, corresponding to *p*-doping/dedoping of a polythiophene backbone, was observed by the wave at about +0.75 V. The relationship between the maximum current peak and the scan rate (varied from 25 to 200 mV s^{-1} was found to be linear (Fig. 8(b)). A linear relationship is typical of a redox-active polymer attached to the electrode and exemplifies the stability of poly-**3** films towards *p*-doping.[65] Scanning negative potentials up to −2.0 V shows several redox waves mainly related to the multiple reduction of the fullerene moiety.[70] The irreversible peak at −0.74 V, of unknown origin, was seen only during the first scans (Fig. 8(a)).[75] Similar to the results found by Ferraris *et al.*,[71,72] these results confirmed that both the polythiophene backbone and the pendant fullerene moieties can substantially retain their individual electrochemical properties. Films of neutral poly-**3** were insoluble, yellow-brownish and not photoluminescent. Their UV-Vis absorption spectra showed a broad feature ranging from about 600 nm to the ITO-glass cut-off, with a shoulder at about 460 nm. As in the case of poly-**1**, this value is significantly blue-shifted as compared to λ_{max} of reference poly-**4**, seen at 530 nm.[75] Again, this has been explained as an effect of the relatively low solubility of monomer **3** (and its oligomer intermediates involved in the electrochemical polymerisation process), leading to a lower molecular weight for the

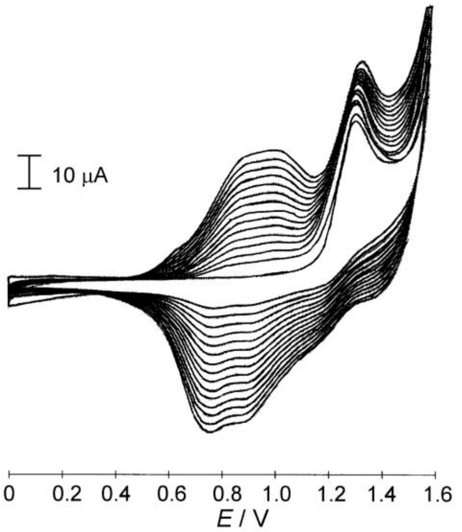


Fig. 7 Anodic cyclic voltammogram of **3** (0.1 M Bu_4NPF_6in CH_2Cl_2). Working electrode: Pt foil; quasi-reference electrode: Ag/AgCl wire (−0.44 V *vs.* ferrocene). Scan rate: 100 mV s^{-1}. (Reproduced from ref. 76 with the permission of the Royal Society of Chemistry.)

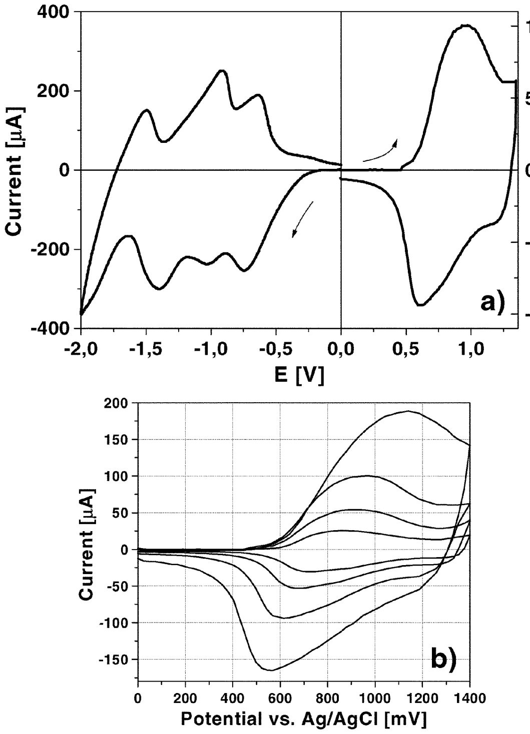


Fig. 8 **a)** Anodic (right) and cathodic (left) cyclic voltammogram of a poly-**3** film (0.1 M Bu_4NPF_6 in acetonitrile), conditions as in Fig. 7. **b)** Anodic cyclic voltammogram of poly-**3** at a scan rate of 25, 50, 100 and 200 mV s^{-1}.

corresponding polymer. According to the electrochemical characterisation, no hints for ground-state donor–acceptor interactions were observed.

The nature of the photoexcitations in poly-**3** solid films was investigated by means of photoinduced absorption (PIA) in the Vis-NIR. The PIA spectrum, taken with excitation at 476 nm, is shown in Fig. 9. Two electronic bands are observed, one with maximum at 1.48 eV and one peaking below 0.6 eV. Both these absorption features compare well with PIA spectra of long oligothiophenes, and were assigned to positive polarons on a thiophene based conjugated backbone.[41,77] Such an assignment was corroborated by comparing these features with those observed by means of PIA-FTIR measurements and *in situ* FTIR spectroelectrochemistry.[75] To shed light on the relaxation kinetics of the photoexcitations, intensity and modulation frequency of the pump beam were varied.[78,79] The polaronic features, evaluated by the signal at 1.38 and 0.62 eV, showed a square root excitation intensity dependence. This indicates non-geminate bimolecular recombination of the photoinduced charges, suggesting the migration of charge carriers with opposite sign to different sites within the films. From the modulation frequency dependence, a broad distribution of charged state lifetimes was observed in the range from 0.8 to 10 ms. While these results prove the photoinduced generation of metastable, positively charged states on the polythiophene backbone, a definitive evidence of a photoinduced electron transfer to the pendant fullerene moieties was obtained by steady-state LESR spectroscopy. The LESR spectrum, calculated by subtracting the "light-off" signal from the "light-on" signal, shows the photogeneration of two paramagnetic species (Fig. 10). The positive polarons on the conjugated backbone were seen by the signal at a *g*-factor of 2.0022, while the signal observed at lower *g*-factor, 2.0004, is typical of fullerene radical-anions.[44,45] As such, it was concluded that in *double-cable* polymers a photoinduced electron transfer from the conjugated backbone to the pendant fullerene moieties can lead to long-lived and mobile charge separated states, as observed earlier in conjugated polymer/fullerene composites.

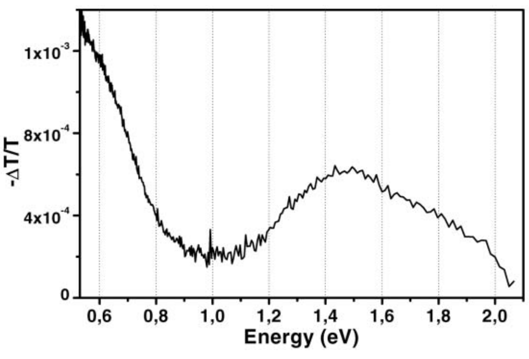


Fig. 9 Photoinduced Vis-NIR absorption of poly-**3** films. Excitation at 476 nm (40 mW on a 4 mm diameter spot). T = 100 K. (Reproduced from ref. 75 with the permission of the American Chemical Society.)

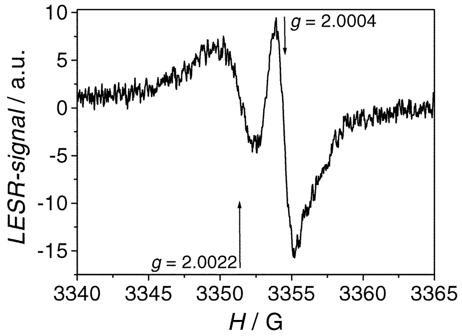


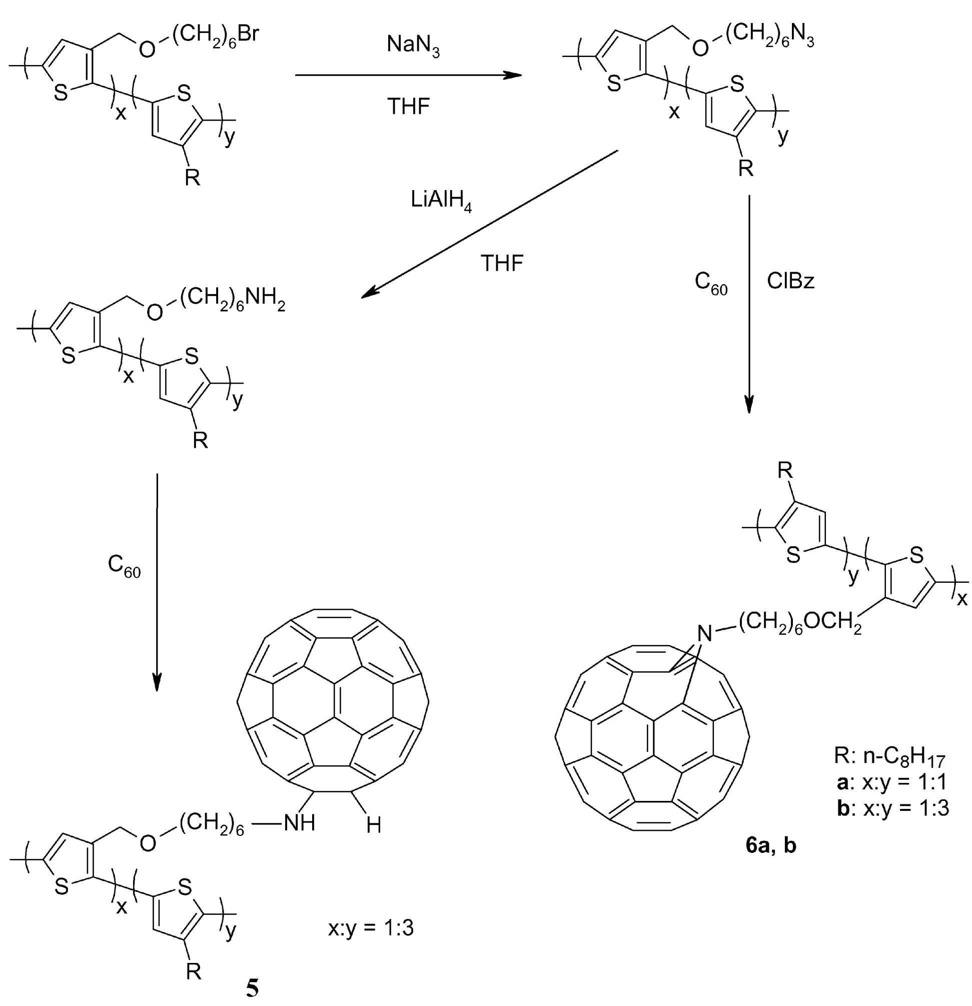
Fig. 10 Integrated LESR (light-on minus light-off) spectrum of poly-**3** on ITO coated plastic foils. Excitation at 488 nm (20 mW cm^{-2}). T = 77 K. (Reproduced from ref. 76 with the permission of the Royal Society of Chemistry.)

4.2 Chemically synthesised soluble double-cable polymers

As already discussed, soluble *double-cable* polymers are required specifically for PV or other electronic applications in thin film devices. The attachment of fullerene moieties to conjugated backbones, which are generally not very soluble, decreases the solubility even more. The design of soluble *double-cables* loaded with an adequate number of fullerene moieties is therefore a very challenging task from the synthetic chemist's point of view. Processable *double-cables* have been prepared following two different approaches:

- the direct reaction of C_{60} with specifically functionalised soluble conjugated polymers;
- the copolymerisation of two monomers, one carrying the fullerene moiety and one designed to improve solubility.

The first approach has been reported by Ferraris *et al.*, in parallel with the preparation of poly-**2**.[72] In this work, head-to-tail co-polyalkylthiophenes containing functionalities as azido- or primary amino-groups were prepared at first (Scheme 4). After treatment with C_{60}, soluble *double-cables* bearing hydrofullerene (**5**) and azafulleroid (**6a**,**b**) moieties were obtained and isolated by extraction. Copolymers **5** and **6b** showed, in solution, absorption spectra peaking at about 438 nm. This value is in rather good agreement with that of standard polythiophenes, and again no absorption at longer wavelengths were observed. *In situ* spectroelectrochemistry measurements upon reduction of **6b** showed the spectroscopic features of the fullerene moiety radical-anions and, at more negative potential, of dianions, according to the results previously reported for fullerenes and azafulleroids.[70,80] At even more negative potentials, the behaviour of copolymer **6b** was similar to that reported for poly-**2**. In the anodic region, the polymer showed the typical *p*-doping/dedoping wave of polythiophenes. As already observed with poly-**2** and poly-**3**,



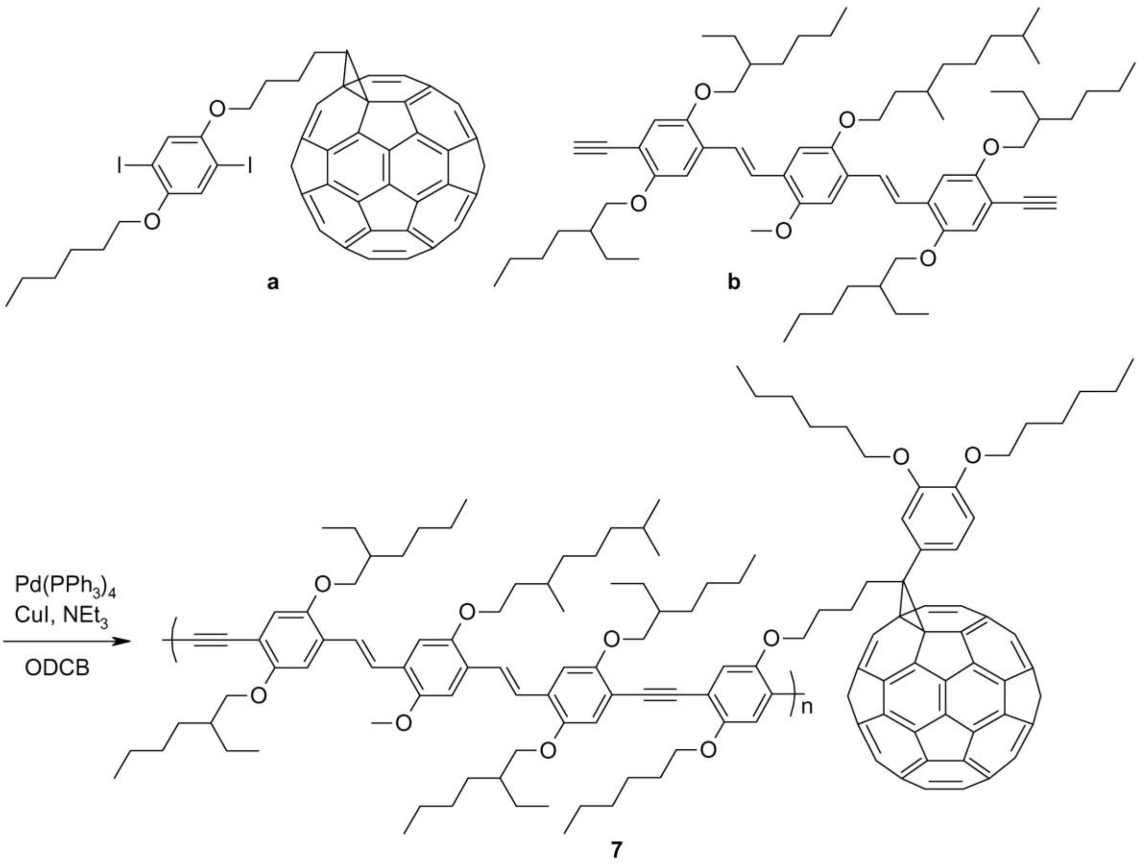
Scheme 4

no hints for a ground-state interaction between the donor and the acceptor moieties were found.

The second approach has been used by Marcos Ramos *et al.*, who have recently reported the preparation of the first solar cell based on a novel *double-cable* polymer.[81,82] They have synthesised a conjugated backbone, hybrid of poly(*p*-phenylene vinylene) and poly(*p*-phenylene ethynylene), with covalently linked methanofullerene moieties (**7**). The synthetic strategy toward **7** is outlined in Scheme 5. The polymer was synthesised under an inert atmosphere in *o*-dichlorobenzene/triethylamine (7 : 3 v/v) *via* a palladium-catalysed cross-coupling of diiodobenzene **a**, bearing a pendant methanofullerene, and oligo-(*p*-phenylene vinylene) **b**, end-capped with reactive ethynylenes. A polymer similar to **7** but lacking the methanofullerene moieties, was used as reference for spectroscopic investigations. The effective conjugation length of the two materials was found to be nearly identical: the $\lambda_{\max}$ of the *double-cable* polymer, found at 468 nm, was 6 nm shifted to blue as compared to that of the reference polymer. The molecular weight of **7** was estimated by size-exclusion chromatography as $M_W = 16200$ (PDI = 2.82). However, there was an indication that this value could be underestimated. Spectroscopic investigations of **7** were done both in solution and in thin solid films. The photoluminescence of **7** in toluene solution was quenched by two orders of magnitude as compared to that of the reference polymer. The quenching of the photoluminescence in apolar solvent involves a singlet–singlet energy transfer from the photoexcited conjugated backbone to the fullerene moieties, as known from studies on oligo(*p*-phenylene vinylene)–fulleropyrrolidine dyads.[60] Photoluminescence quenching was observed also in thin solid films. However, in this case, the quenching mechanism is the photoinduced electron transfer as discussed before. Accordingly, the photoinduced Vis-NIR absorption spectrum of **7** in the solid state exhibits the band typical of methanofullerene radical-anions at about 1.2 eV (this fullerene radical-anion feature was not seen in the poly-**3** spectrum due to the concomitant onset of the broad and much more intense polaron absorption band of the polymer) accompanied by two broad bands, seen at 0.62 and 1.53 eV, characteristic of positive polarons on a conjugated chain (Fig. 11). As reported for poly-**3**, the photoinduced charge recombination was found to follow non-geminate bimolecular kinetics. The lifetime of the photogenerated charges in **7** also extends to the millisecond time domain.

Photovoltaic elements were prepared by spin-coating **7** from chloroform solution.[81] The current voltage (*I*/*V*) curves of the device recorded in the dark and under white-light illumination (100 mW cm^{-2}) revealed a J_{SC} value of 0.42 mA cm^{-2}, a V_{OC} of 830 mV, and a (FF) of 0.29 (Fig. 12). The IPCE showed an onset at 550 nm and a maximum of 6% at 480 nm. It is worthy of note that the performance of this first example of *double-cable* based solar cells, which were not optimised, is already competitive to that of devices prepared following the *p*/*n*-heterojunction as well as the "bulk-heterojunction" approaches.[27,83,84] Moreover, this performance is given by a *double-cable* with a fullerene loading of 31.5 wt%, a value considerably smaller than that used commonly in "bulk-heterojunction" solar cells (about 75 wt%).

Another interesting family of soluble *double-cable* copolythiophenes carrying fulleropyrrolidine moieties as well as solubilising chains (**8a**,**b**) has been reported recently by Zhang *et al.*[85] These random copolymers were prepared by



Scheme 5

chemical oxidative coupling, adding a slurry of $FeCl_3$ in chloroform to the monomers dissolved in the same solvent. Two differently fullerene-loaded copolymers were prepared by using two different solubilising- monomer (**b**)/fullerene-bearing monomer (**a**, prepared *via* the Prato's reaction) ratios in the feed (see Scheme 6). After dedoping and removal of low molecular weight fractions and byproducts, the copolymers were found to contain 7 mol% (corresponding to 14.5 wt%, **8a**) and 14 mol% (corresponding to 24.2 wt%, **8b**) of fullerene monomer, respectively. Size exclusion chromatography in chloroform gave the following molecular weights: M_W = 48000, M_N = 28000 for **8a**, M_W = 39000, M_N = 26000 for **8b**. When higher percentages of fullerene monomer were placed in the feed, an insoluble material was obtained. The solubilising monomer used in excess in this preparation leads, when used alone, to a polythiophene known as PEOPT (see Chart). PEOPT spin-coated from chloroform solution leads to an orange-phase. This phase can be converted to a more ordered blue-phase by thermal annealing or by chloroform vapours exposure.[47,86] Although the presence of the bulky fullerene moieties, also **8a** and **8b** retain such a property. Both copolymers undergo colour change from orange to blue upon exposure to chloroform vapours at room temperature. In this blue-phase, both copolymers display a broad electronic absorption band covering a wide range of the solar spectrum, which is in itself an interesting property for PV materials.

The solubility of **8a** and **8b** allowed the fabrication of photodiodes.[85] In these devices, the thickness of the photoactive layer was 70 nm and the active area was 4 mm^2. The devices based on the more fullerene loaded *double-cable* **8b** showed an IPCE more than twofold higher as compared to that of the devices prepared with **8a** (Fig. 13). A significant

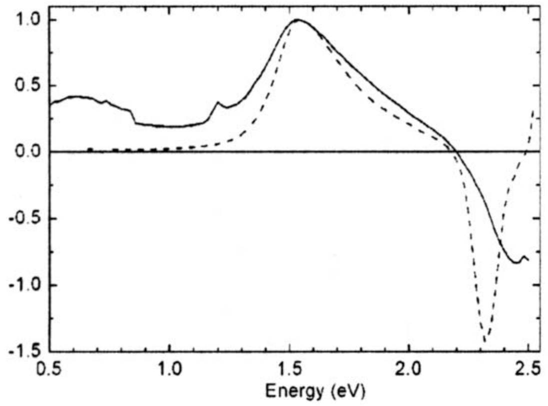


Fig. 11 Photoinduced Vis-NIR absorption spectra of **7** (solid line) and of the reference polymer without fullerene moieties (dashed line) on quartz. T = 80 K. (Reproduced from ref. 81 with the permission of the American Chemical Society.)

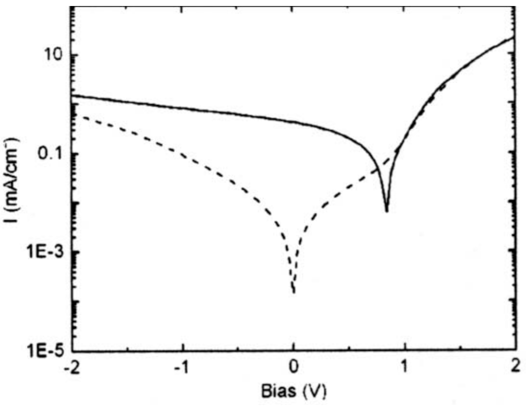
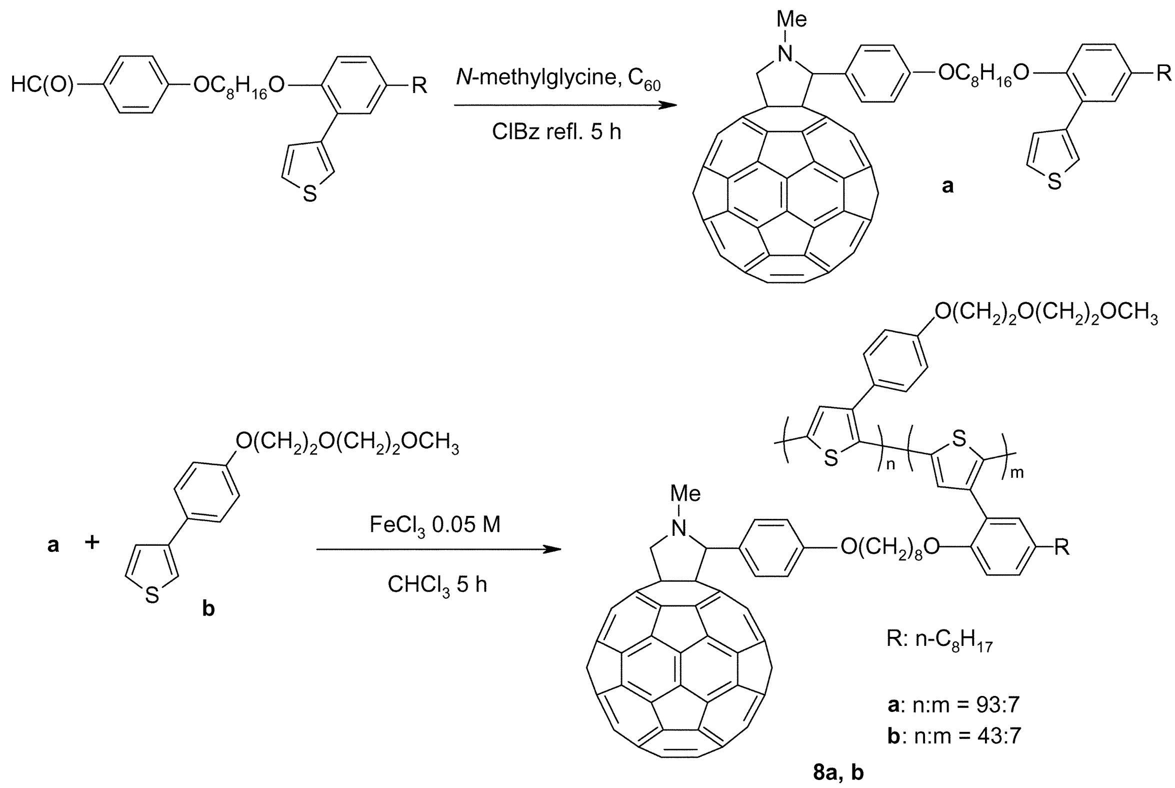


Fig. 12 Current voltage characteristics of an ITO/PEDOT:PSS/**7**/Al device in the dark (dashed line) and under white-light illumination (solid line). (Reproduced from ref. 81 with the permission of the American Chemical Society.)



Scheme 6

improvement of the IPCE was obtained in both cases after treating the photoactive films with chloroform just before evaporation of the Al electrode. This effect reflects the change in the absorption spectra while going from the orange- to the blue-phase of the copolymers. The devices prepared using **8b** where characterised under monochromatic light ($\lambda = 505$ nm) illumination with an intensity of 0.1 mW cm^{-2}. The FF was 0.25 and the power conversion efficiency was 0.6%.[50] The diodes not treated with chloroform vapour gave the highest photovoltages, $V_{OC} = 750$ mV. This value is higher than that reported for PEOPT/C_{60} "bulk-heterojunction" solar cells.[47] After treatment with chloroform vapours, the V_{OC} of the device dropped to 450 mV. This behaviour is a consequence of the altered energy levels between the orange- and the blue-phases.[37,46,85]

Another class of soluble *double-cables* has been described by Xiao *et al.*[87] and by Wang *et al.*[88] Based on the well established photoconducting as well as electrochemical properties of carbazole, they synthesised a soluble regular copolymer containing *p*-phenylene vinylene and carbazole units, the latter bearing a pendant azido functionality. The reaction with C_{60} in chlorobenzene gave a soluble fraction (CCl_4) with a fullerene percentage estimated spectroscopically as 19.9 wt%. (**9**). In a similar way, they synthesised a *double-cable* containing also triphenylamine moieties (**10**). In this case, the fullerene content was about 21 wt%. The weight-average M_W values were determined by means of gel permeation chromatography as 3810 for **9** and 5051 for **10**. Based on these values, it is clear that these *double-cables* consist of only few repeating units. A highly fullerene loaded *double-cable* has been prepared by the same group (**11**).[88] In this latter material, the fullerene percentage has been estimated as high as 68.8 wt%. This value seems to be overestimated, since based on the repeating unit the calculated maximum fullerene loading is *ca.* 57 wt%. Nevertheless, this is a high fullerene loading, approaching that of conjugated polymer/fullerene composites used for the fabrication of "bulk-heterojunction" solar cells with improved efficiency. By means of thermal gravimetric analysis, these copolymers have been found to be stable up to about 350 °C, and moderate weight losses occurred just within the range 380–460 °C. Spectroscopic and electrochemical studies allowed the authors to conclude that the electronic properties of the fullerene moieties were substantially preserved in all cases. Photoinduced electron transfer has been claimed to occur due to photoluminescence quenching observed in chloroform solutions. These *double-cable* polymers are currently tested as material for plastic PV energy conversion.[88]

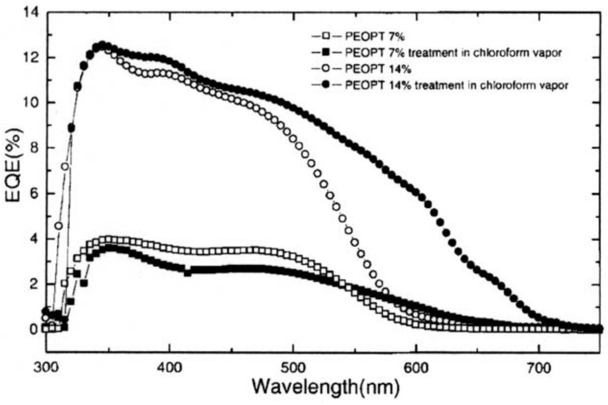
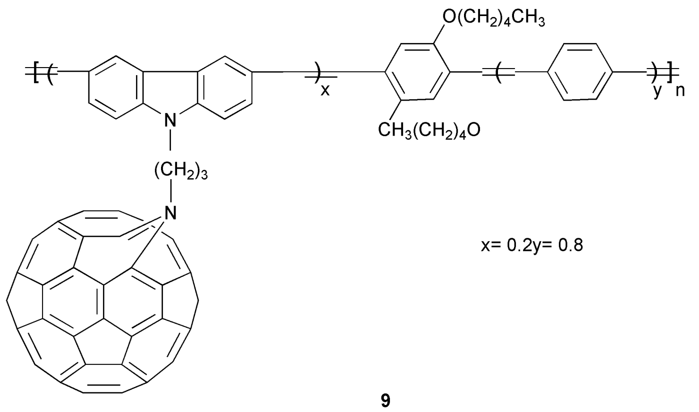


Fig. 13 External quantum efficiency (IPCE) of ITO/PEDOT:PSS/**8a** or **8b**/Al photodiodes under monochromatic light illumination, prior to, and after, conversion from the orange- to the blue-phase. (Reproduced from ref. 85 with the permission of WILEY-VCH.)

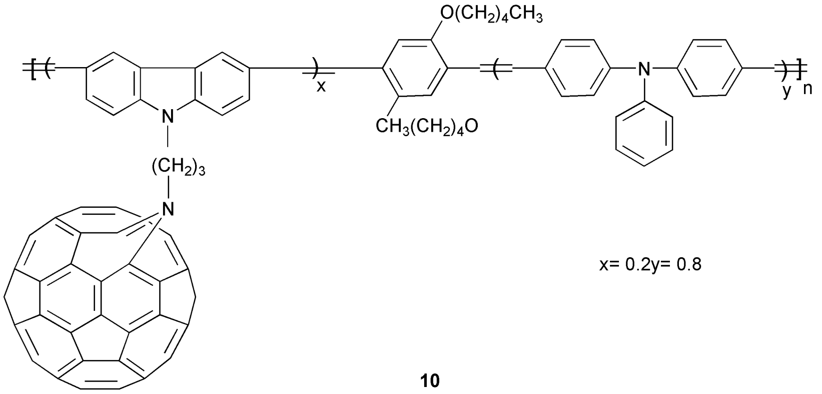
5 Conclusions and perspectives

Preparation and properties of a novel class of fullerene functional materials such as *double-cable* polymers have been reviewed. These materials consist of a hole conducting, conjugated backbone (*p*-cable) with covalently bound fullerene moieties (*n*-cable). By the choice of the proper covalent linkage, the donor and the acceptor moieties can be electronically "isolated" to exclude ground-state interactions. As such, *double-cable* polymers are attractive for all organic electronic



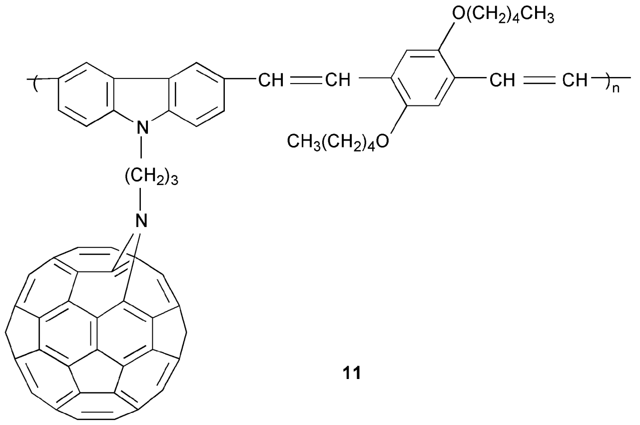
x= 0.2y= 0.8

9



x= 0.2y= 0.8

10



11

applications in which bipolar transport is required. Photoexcitation spectroscopic investigations have shown that *double-cables* in their solid state undergo photoinduced electron transfer, leading to long-lived, mobile charge carriers as observed earlier in conjugated polymer/fullerene composites. Since in *double-cable* polymers phase separation cannot occur, these materials are indeed appealing as a way to control both electronic and morphological properties within the photoactive layer of plastic solar cells. The very important technological issue is processability, which is certainly the major challenge towards practical application of *double-cables* polymers in thin film devices. With the few soluble *double-cable* polymers prepared so far, the fabrication of prototype photodiodes and solar cells has been demonstrated. However, in the *double-cable* approach a compromise between the fullerene loading (for the transport of electrons) and solubility has been made. With this respect:

- improving the design of the synthesis may allow the preparation of processable materials with acceptably high fullerene moieties percentage as well as acceptable solubility;
- fullerene loading as high as 14 mol% (24.2 wt%, **8b**) has been obtained in a soluble random copolymer, and a loading of 31.5 wt% has been already obtained even in a polymer with well-defined backbone (**7**);
- Balberg *et al.* have reported bipolar transport in a poly-(3-hexylthiophene)/C_{60} composite with a fullerene fraction of 10 mol%.[89] Indeed, it can be considered that the volume fraction occupied by the fullerene moieties of a *double-cable* could be enhanced if the volume occupied by the solubilising but electrically inactive chains would be minimised;
- the *double-cable* concept may lead to bipolar transport properties even in guest–host systems where the *double-cable* polymer is embedded within processable polymers as matrices;
- synthetic strategies toward fullerene derivatives able to self-assemble with suitably designed conjugated polymers should be considered as an alternative to covalently bound *double-cables*, too. To this end, self-assembly strategies based on electrostatically driven or other key–lock interactions should be possible.[90–92]

Finally, we would like to mention self-organization also as an interesting possibility to control the morphology of the photoactive film. In this respect, covalently linked *double-cable* polymers could be further functionalised, for example with amphiphilic substituents, to gain additional control of the final morphology by their tertiary structure.[90–93]

Acknowledgement

We thank C. J. Brabec, H. Neugebauer and G. Zerza for many helpful discussions. Studies on the *double-cable* polymers in Linz have been carried out within the JOULE III Project "Molecular Plastic Solar Cells", funded by the European Commission, Contract No. JOR3CT980206. We gratefully acknowledge our collaboration partners within this consortium: M. R. Andersson and M. Svensson (Chalmers University of Technology, Sweden), E. Ehrenfreund (Technion, Israel), D. Fainman (Ben Gurion University of Negev, Israel), E. Glötzl (QSEL, Austria), J. C. "Kees" Hummelen (University of Groningen, The Netherlands), O. Inganäs (Linköping University, Sweden), R. A. J. Janssen (TU Eindhoven, The Netherlands), M. Maggini, S. Bucella (University of Padova, Italy), N. Martín, R. Gómez and J. L. Segura (Universidad Complutense de Madrid, Spain), M. Prato (University of Trieste, Italy).

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
2 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Hufman, *Nature*, 1990, **347**, 354.
3 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996.
4 F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317.
5 A. Hirsch, in *Fullerenes and Related Structures, Topics in Current Chemistry*, Springer-Verlag, Berlin, 1999, Vol. 199.
6 J. L. Segura and N. Martín, *J. Mater. Chem.*, 2000, 2403, and references therein.
7 M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097, and references therein.
8 K. Kadish and R. Ruoff, Eds., *Fullerenes: Chemistry, Physics and Technology*, Wiley Interscience, 2000.
9 A. J. Heeger, *J. Phys. Chem. B*, 2001, **105**, 8475.
10 H. S. Nalwa, Ed., *Handbook of Conductive Molecules and Polymers,* Wiley, Chichester, 1997, Vol. 1–4.
11 T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Eds., *Handbook of Conducting Polymers*, 2nd edition, Marcel Dekker, New York, 1998.
12 G. Hadziioannu and P. F. van Hutten, Eds., *Semiconducting Polymers, Chemistry Physics and Engineering,* Wiley, Weinheim, 2000.
13 J. H. Burroughs, D. D. C. Bradley, A. B. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.
14 G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature* (London), 1992, **357**, 477.
15 G. Grem, G. Leditzky, B. Ulrich and G. Leising, *Adv. Mater.*, 1992, **4**, 36.
16 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
17 N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474.
18 S. Morita, A. A. Zakhidov and K. Yoshino, *Solid State Commun.*, 1992, **82**, 249.
19 N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky and F. Wudl, *Appl. Phys. Lett.*, 1993, **62**, 585.
20 G. Yu, J. Wang, J. McElvain and A. J. Heeger, *Adv. Mater.*, 1998, **10**, 1431.
21 H. Meier, *Organic Semiconductors*, Verlag-Chemie, Weinheim, 1974.
22 C. W. Tang, *Appl. Phys. Lett.*, 1986, **48**, 183.
23 J. Simon and J.-J. André, *Molecular Semiconductors*, Springer, Berlin, 1985.
24 M. Kaneko, in, *Handbook of Conductive Molecules and Polymers,* Ed. H. S. Nalwa, Wiley, Chichester, 1997, Vol. 4, p. 661.
25 J. Rostalski and D. Meissner, *Sol. Energy Mater. Sol. Cells*, 2000, **61**, 87.
26 T. Tsuzuki, Y. Shirota, J. Rostalski and D. Meissner, *Sol. Energy Mater. Sol. Cells*, 2000, **61**, 1.
27 C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 15, and references therein.
28 G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789.
29 S. E. Shaheen, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen and N. S. Sariciftci, *Appl. Phys. Lett.*, 2001, **78**, 841.
30 Y. Wang and A. Suna, *J. Phys. Chem. B*, 1997, **101**, 5627.
31 J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **270**, 1789.
32 G. Yu and A. J. Heeger, *J. Appl. Phys.*, 1995, **78**, 4510.
33 G. Zerza, M. C. Scharber, C. J. Brabec, N. S. Sariciftci, R. Gómez, J. L. Segura, N. Martín and V. I. Srdanov, *J. Phys. Chem. A*, 2000, **104**, 8315.
34 T. Yohannes, H. Neugebauer, S. A. Jenekhe and N. S. Sariciftci, *Synth. Met.*, 2001, **116**, 241.
35 G. Zerza, A. Cravino, H. Neugebauer, N. S. Sariciftci, R. Gómez, J. L. Segura, N. Martín, M. Svensson and M. R. Andersson, *J. Phys. Chem. A*, 2001, **105**, 4172.
36 P. J. Skabara, I. Serebrykov, I. Perepichka, N. S. Sariciftci, H. Neugebauer and A. Cravino, *Macromolecules*, 2001, **34**, 2232.
37 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374.
38 H. Neugebauer, C. J. Brabec, J. C. Hummelen and N. S. Sariciftci, *Sol. Energy Mater. Sol. Cells*, 2000, **61**, 35.
39 N. S. Sariciftci, Ed. *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton* versus *Semiconductor Band Model,* World Scientific, Singapore, 1997.
40 See, for instance, R. Menon, C. O. Yoon, D. Moses and A. J. Heeger, in *Handbook of Conductive Molecules and Polymers,* Ed. H. S. Nalwa, Wiley, Chichester, 1997, Vol. 1, ch. 2, and references therein.
41 L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger and F. Wudl, *J. Phys. Chem. B*, 1993, **47**, 13835.
42 C. J. Brabec, G. Zerza, G. Cerullo, S. De Silvestri, S. Luzzati, J. C. Hummelen and N. S. Sariciftci, *Chem. Phys. Lett.*, 2001, **340**, 232.
43 C. H. Lee, G. Yu, N. S. Sariciftci, D. Moses, K. Pakbaz, C. Zhang, A. J. Heeger and F. Wudl, *Phys. Rev. B*, 1993, **48**, 15425.
44 P. M. Allemand, G. Srdanov, A. Koch, K. Khemeni, F. Wudl, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Am. Chem. Soc.*, 1991, **113**, 2780.
45 V. Dyakonov, G. Zoriniants, M. C. Scharber, C. J. Brabec, R. A. J. Janssen, J. C. Hummelen and N. S. Sariciftci, *Phys. Rev. B*, 1999, **59**, 8019.
46 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, M. T. Rispens, L. Sanchez, J. C. Hummelen and T. Fromherz, *Thin Solid Films*, 2002, **403–404**, 368.
47 L. S. Roman, W. Mammo, L. A. A. Petersson, M. R. Andersson and O. Inganäs, *Adv. Mater.*, 1998, **10**, 774.
48 J. J. M. Halls and R. H. Friend, *Synth. Met.*, 1997, **85**, 1307.
49 T. Martens, J. D'Haen, T. Munters, L. Goris, Z. Beelen, J. Manca, M. D'Olieslaeger, D. Vanderzande, L. De Schepper and R. Andriessen, *MRS Proc.*, in press.
50 The fill factor (FF) of a solar cell is determined as FF $= I_{\mathrm{mpp}}V_{\mathrm{mpp}}/I_{\mathrm{SC}}V_{\mathrm{OC}}$, where I_{mpp} and V_{mpp} are the current and the voltage at the maximum power point in the fourth quadrant of the I/V curve. The power-in to power-out conversion efficiency η is given by $\eta = I_{\mathrm{SC}}V_{\mathrm{OC}}\mathrm{FF}/I_{\mathrm{light}}$, where I_{light} is the intensity of the incident light. AM1.5 illumination conditions correspond to the global sunlight spectrum, with $I_{\mathrm{light}} = 860$ W m^{-2}. An interesting discussion on the usefulness of different kinds of given efficiency values can be found in ref. 25.
51 W. Geens, S. E. Shaeen, C. J. Brabec, J. Poortmans and N. S. Sariciftci, in *Electronic Properties of Novel Materials,* Eds., H. Kuzmany, J. Fink, M. Mehring and S. Roth, IOP, Bristol, Vol. 544, 2000, 516.
52 U. Stalmach, B. de Boer, C. Videlot, P. F. van Hutten and G. Hadziioannou, *J. Am. Chem. Soc.*, 2000, **122**, 5464.
53 N. Martín, L. Sanchez, B. Mescas and I. Pérez, *Chem. Rev.*, 1998, **98**, 2527.
54 S.-G. Liu, L. Shu, J. Rivera, H. Liu, J.-M. Raimundo, J. Roncali, A. Gorgues and L. Echegoyen, *J. Org. Chem.*, 1999, **64**, 4884.
55 S. Knorr, A. Grupp, M. Mehring, G. Grube and F. Effenberger, *J. Chem. Phys. A*, 1999, **110**, 3502.
56 T. Yamashiro, Y. Aso, T. Otsubo, H. Tang, Y. Harima and K. Yamashita, *Chem. Lett.*, 1999, 443.
57 J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. V. Krasnikov and G. Hadziioannou, *Chem. Commun.*, 1999, 617.
58 P. A. van Hal, J. Knol, B. M. W. Langeveld-Voss, S. C. J. Meskers, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. A*, 2000, **104**, 5974.
59 N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud and J.-F. Nierengarten, *Chem. Commun.*, 2000, 599.
60 E. Peeters, P. A. van Hal, J. Knol, C. J. Brabec, N. S. Sariciftci, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. B*, 2000, **104**, 10174.
61 J. L. Segura, R. Gómez, N. Martín, C. Luo and D. M. Guldi, *Chem. Commun.*, 2000, 701.
62 I. B. Martini, B. Ma, T. Da Ros, R. Helgeson, F. Wudl and B. Schwartz, *Chem. Phys. Lett.*, 2000, **327**, 253.
63 A. Cravino, C. J. Brabec, A. Y. Andreev, R. Rittberger, N. S. Sariciftci, E. Peeters, R. A. J. Janssen, J. Knol and J. C. Hummelen, presented at MRS 2000 Fall Meeting, Cluster 8: Organic and Biomaterials; Symposium JJ: Organic Electronic and Photonic Materials and Devices. Boston, 27th Nov.–1st Dec., 2000.
64 C. J. Brabec, *et al.*, manuscript in preparation.
65 J. Simonet and J. Rault Berthelot, *Prog. Solid State Chem.*, 1991, **21**, 1.

66 J. Roncali, *J. Mater. Chem.*, 1999, **9**, 1875, and references therein.
67 J. Roncali, *J. Mater. Chem.*, 1999, **9**, p. 1888.
68 European Commision, Joule III program for Molecular Plastic Solar Cells, Contract No. JOR3CT980206.
69 T. Benincori, E. Brenna, F. Sannicoló, L. Trimarco and G. Zotti, *Angew. Chem.*, 1996, **108**, 718.
70 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.
71 A. Yassar, M. Hmyene, D. C. Loveday and J. P. Ferraris, *Synth. Met.*, 1997, **84**, 231.
72 J. P. Ferraris, A. Yassar, D. Loveday and M. Hmyene, *Optical Materials (Amsterdam)*, 1998, **9**, 34.
73 D. Gebeheyu, F. Padinger, T. Fromherz, J. C. Hummelen and N. S. Sariciftci, *Int. J. Photoenergy*, 1999, **1**, 95.
74 D. Gebeheyu, F. Padinger, T. Fromherz, J. C. Hummelen and N. S. Sariciftci, *Bull. Chem. Soc. Ethiop.*, 2000, **14**, 57.
75 A. Cravino, G. Zerza, H. Neugebauer, M. Maggini, S. Bucella, E. Menna, M. Svensson, M. R. Andersson, C. J. Brabec and N. S. Sariciftci, *J. Phys. Chem. B*, 2002, **106**, 70.
76 A. Cravino, G. Zerza, M. Maggini, S. Bucella, M. Svensson, M. R. Andersson, H. Neugebauer and N. S. Sariciftci, *Chem. Commun.*, 2000, 2487.
77 R. A. J. Janssen, D. Moses and N. S. Sariciftci, *J. Chem. Phys.*, 1996, **101**, 9519.
78 G. Dellepiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi and A. Borghesi, *Phys. Rev. B*, 1993, **48**, 7850.
79 C. Botta, S. Luzzati, R. Tubino, D. D. C. Bradley and R. H. Friend, *Phys. Rev. B*, 1993, **48**, 14809.
80 M. K. Mazen, R. T. Carlin, P. C. Trulove, G. R. Eaton and S. S. Eaton, *J. Am. Chem. Soc.*, 1994, **116**, 3465.
81 A. Marcos Ramos, M. T. Rispens, J. K. J. van Duren, J. C. Hummelen and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2001, **123**, 6714.
82 A. Marcos Ramos, M. T. Rispens, J. C. Hummelen and R. A. J. Janssen, *Synth. Met.*, 2001, **119**, 171.
83 L. S. Roman, M. R. Andersson, T. Yohannes and O. Inganäs, *Adv. Mater.*, 1997, **9**, 1164.
84 H. Matoussi, M. F. Rubner, F. Zhou, J. Kumar, S. K. Tripathy and L. Y. Chiang, *Appl. Phys. Lett.*, 2000, **77**, 1540.
85 F. Zhang, M. Svensson, M. R. Andersson, M. Maggini, S. Bucella, E. Menna and O. Inganäs, *Adv. Mater.*, 2001, **13**, 171.
86 C. J. Brabec, C. Winder, M. C. Scharber, N. S. Sariciftci, J. C. Hummelen, M. Svensson and M. R. Andersson, *J. Chem. Phys.*, 2001, **115**, 7235.
87 S. Xiao, S. Wang, H. Fang, Y. Li, Z. Shi, C. Du and D. Zhu, *Macromol. Rapid. Commun.*, 2001, **22**, 1313.
88 S. Wang, S. Xiao, Y. Li, Z. Shi, C. Du, H. Fang and D. Zhu, *Polymer*, 2002, **43**, 2049.
89 I. Balberg, R. Naidis, M.-K. Lee, J. Shinar and L. F. Fonseca, *Appl. Phys. Lett.*, 2001, **79**, 197.
90 M. T. Rispens, L. Sánchez, J. Knool and J. C. Hummelen, *Chem. Commun.*, 2001, 161.
91 J. J. González, S. González, E. M. Prego, C. Luo, D. M. Guldi, J. de Mendoza and N. Martín, *Chem. Commun.*, 2001, 163.
92 S. Mizyed, P. E. Georghiou, M. Barcu, B. Cuadra, A. K. Rai, P. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 2001, **123**, 12770.
93 S. A. Jenekhe and X. L. Chen, *Science*, 1998, **279**, 1903.