

# Linear $\pi$ -conjugated systems derivatized with $C_{60}$ -fullerene as molecular heterojunctions for organic photovoltaics

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This *tutorial review* covers recent contributions in the area of linear  $\pi$ -conjugated systems bound to fullerenes in view of their application as active materials in photovoltaic devices. The first part discusses the concepts of double-cable polymer and molecular hetero-junction and presents several examples of chemically or electrochemically synthesized  $C_{60}$ -derivatized conjugated polymers. The second and main part of the article concerns the various classes of  $C_{60}$ -derivatized  $\pi$ -conjugated oligomers designed in view of their utilization in single-component photovoltaic devices. Thus,  $C_{60}$ -containing  $\pi$ -conjugated systems such as oligoarylenevinylenes, oligoaryleneethynylenes and oligothiophenes are discussed on the basis of the relationships between molecular structure, photophysical properties and performances of the derived photovoltaic devices. A brief last section presents some recent examples of surface-attached molecular hetero-junctions based on self-assembled monolayers and discusses possible routes for future research.

## 1 Introduction

The realization of the first organic light-emitting devices (OLED) in which a  $\pi$ -conjugated polymer was used as luminophore in 1990<sup>1</sup> and the rapid intensification of research on organic field effect transistors<sup>2</sup> (OFET) based on  $\pi$ -conjugated systems have generated a considerable interest in organic semi-conductors from both fundamental and technological viewpoints. Furthermore, the recent association of organic semi-conductors with flexible substrates such as polymer films or paper has led to the emergence of the field of plastic electronics which is acquiring a growing importance motivated by large industrial perspectives. In fact, organic semi-conductors offer the possibility of developing light-weight, low-cost, and eventually disposable products such as intelligent paper, flexible display devices, tags or

RFID by means of rather simple and low-energy demanding technologies.

Whereas OLED and OFET provide the basic tools for signal processing and data display, a third type of component is required in order to supply energy to the two former systems. Thus, while in the long term, organic photovoltaic devices may contribute to the development of renewable energy sources in the general context created by environmental concerns and the predictable exhaustion of fossil energy resources, in the shorter term organic solar cells may find a niche as an energy source in the emerging area of plastic electronic devices.

Although for almost two decades organic solar cells have essentially remained a subject of basic research, the impressive progress accomplished in the performances of organic photovoltaic devices in the past few years has deeply changed our view of the subject making the realization of organic solar cells a credible industrial objective.

Hetero-junctions based on the association of donor (p-type) and acceptor (n-type) molecular or polymeric  $\pi$ -conjugated systems represent the most efficient configuration to realize organic photovoltaic cells with high power conversion efficiency. In their most basic configuration, organic hetero-junction solar cells are formed by the superposition of two layers of donor and acceptor materials.<sup>3,4</sup> In such bi-layer systems, the dissociation of photo-generated excitons occurs at the interface between the donor and acceptor material and conversion efficiency is thus limited by the average exciton diffusion length, which in turn determines the maximum possible thickness of the active interfacial zone.<sup>4</sup>

Under these circumstances, the improvement of the efficiency of hetero-junction cells can be considered through two different approaches. The first and more long-term one resorts to the synthesis of new p-type and n-type organic semi-conductors specifically designed for photovoltaic conversion. Such materials should ideally combine a band gap engineered for optimal absorption of the solar irradiation spectrum, large



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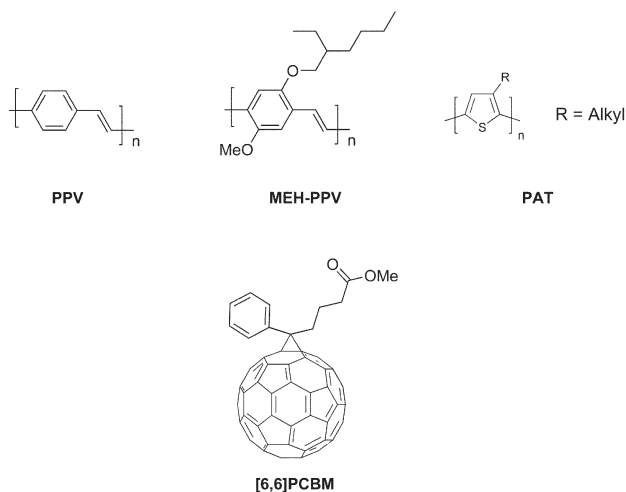
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exciton diffusion length and high holes or electrons mobility. Among other factors, such hypothetical optimized active materials would improve the power conversion efficiency of the solar cells by allowing an increase of the depth of the interfacial active zone. An “horizontal” alternative to this “vertical” or “in depth” approach involves an increase of the number of photo-generated charge-carriers by enlarging the contact area between the p-type and n-type materials of the hetero-junction. Such an objective can be pursued by the development of nano-structured active materials presenting a large surface-to-volume ratio. This concept was initially proposed and developed by Grätzel and coworkers in the case of hybrid organic–inorganic dye-sensitized solar cells.<sup>5</sup> In such a cell the junction is formed at the interface between nano-structured titanium dioxide, a wide band gap n-type inorganic semi-conductor, and a chemisorbed monolayer of a ruthenium tris(bipyridyl) complex which acts as photon harvesting and electron donor component. A major advantage of this cell design is that a sintered film of 15 nm thickness of nanocrystalline TiO<sub>2</sub> particles has an active area *ca.* 1000 times larger than its geometrical area, thus allowing an adsorbed monolayer of appropriate sensitizer to absorb 99% of the incident light. Although these hybrid solar cells can reach power conversion efficiencies approaching 10%, the need for a liquid electrolyte for transporting the photo-generated holes remains a major obstacle to industrial development.

A different and more recent illustration of the concept of bulk hetero-junction involves photovoltaic cells based on blends of conjugated polymers and soluble fullerene C<sub>60</sub> derivatives. In 1991, it was reported that solvent-cast films of C<sub>60</sub> fullerene were able to generate a photocurrent in a photo-electrochemical cell using the iodide/iodine couple for hole transport.<sup>6</sup> Shortly after, Sariciftci *et al.* demonstrated that photo-excitation of a mixture of a  $\pi$ -conjugated polymer, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV), and C<sub>60</sub> fullerene resulted in an ultra-fast photo-induced electron transfer from the  $\pi$ -conjugated system to C<sub>60</sub> with a quantum efficiency for charge separation close to unity.<sup>7</sup> Furthermore, the long lifetime (up to the millisecond-range) of the metastable charge-separated state associated with the delocalization of the positive and negative charge over the  $\pi$ -conjugated system and the fullerene group respectively allows both efficient charge transport and charge collection at the electrodes.<sup>8,9</sup> Besides an almost quantitative photo-induced electron transfer process, the high power conversion efficiency of solar cells based on composite materials of  $\pi$ -conjugated systems and C<sub>60</sub> lies primarily in the formation of a large contact area interfacial hetero-junction between the donor and acceptor in the hybrid material.<sup>8,9</sup>

During the past ten years, organic solar cells based on interpenetrated networks of a soluble C<sub>60</sub> derivative, namely 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]methanofullerene (PCBM), and conjugated polymers such as poly(*para*-phenylenevinylene) (PPV), poly[methoxy(ethylhexyl)-*para*-phenylenevinylene] (MEHPPV) or more recently poly(3-alkylthiophenes) (PAT) have been a focus of intensive research efforts focused both on the analysis of the elemental mechanisms involved in the photon/electron conversion process and on the optimization of the technology of device fabrication.<sup>9</sup>



These synergistic research efforts have generated a continuous improvement of the performances of the cells which now reach power conversion efficiencies up to 2.5% and 3% for cells based on PPV or poly(3-alkylthiophenes) respectively.<sup>9</sup>

Work carried out in different groups has provided clear evidence of the critical importance of morphological aspects to the quality of the junction and hence to the final output performances of the devices.<sup>9,10</sup> In particular it has been shown that the limited miscibility of the two components in the biphasic system can lead to the formation of clusters of fullerene. Such a process which limits the efficiency of charge transport underlines the key role of the solvent used for the preparation of the composite film.<sup>9,10</sup>

While stimulating further research on the technology of organic bulk hetero-junction solar cells, these results have also provided a strong incitement for the development of alternative approaches. In this context, the covalent fixation of the C<sub>60</sub> group on the  $\pi$ -conjugated system has progressively emerged as a very active field of research. In fact, in addition to a possible answer to the problem of phase segregation and clustering phenomena, such an approach could, at a more advanced stage, provide new synthetic tools for a more global control of the interface between the  $\pi$ -conjugated donor and the fullerene acceptor, thus allowing a fine tuning of relevant parameters such as the ratio, distance, relative orientation and mode of connection of the donor and acceptor groups. Furthermore, in addition to interesting model systems for the analysis of the fundamental aspects of photo-induced charge generation, C<sub>60</sub>-derivatized  $\pi$ -conjugated systems can open interesting opportunities to develop nanoscale or molecular photovoltaic devices.

The aim of this article is to present a brief overview of various facets of this area in order to try to identify some possible future directions of research.

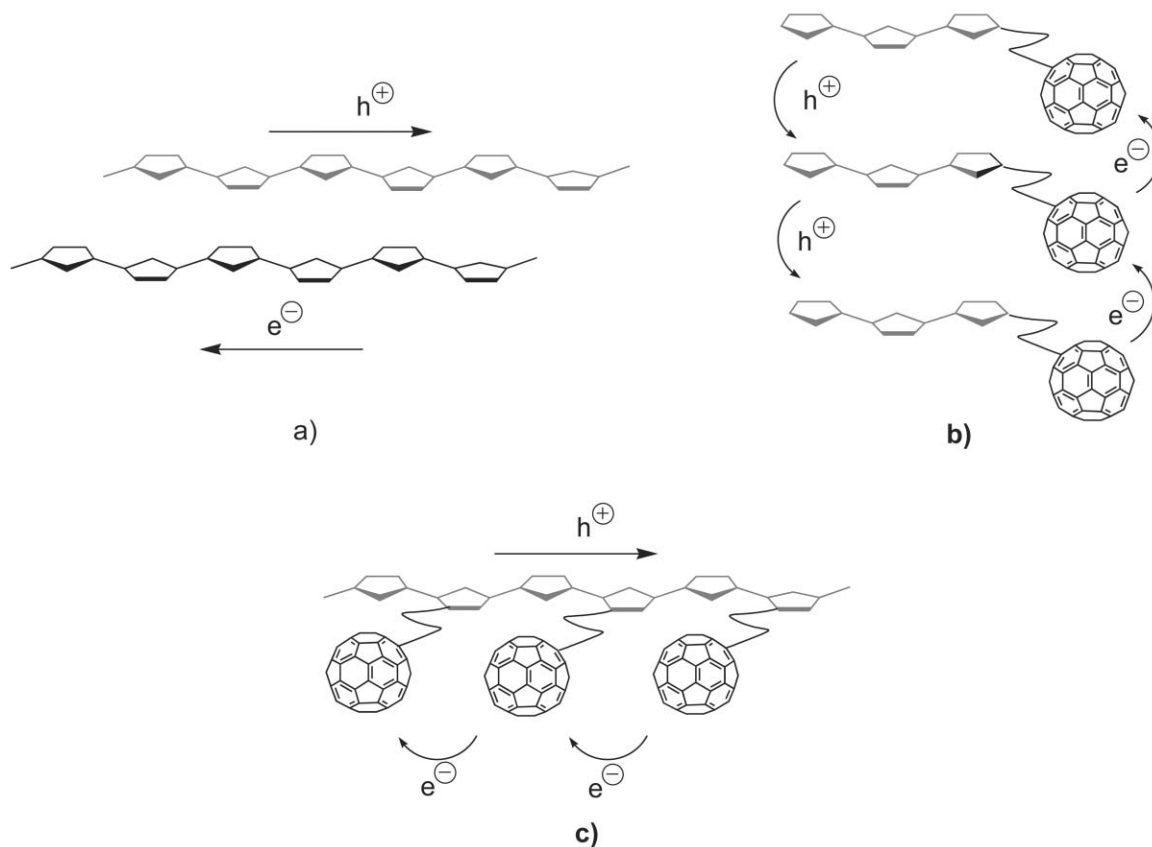
## 2 C<sub>60</sub>-derivatized linear $\pi$ -conjugated systems: “double cable” polymers and molecular hetero-junctions

The tremendous development of the chemistry of fullerenes during the past decade has given rise to the synthesis of a huge

number of dyads consisting of donor groups covalently attached onto  $C_{60}$ .<sup>11</sup> Although many of these compounds have been considered as model systems for the analysis of photo-induced energy or charge transfer processes, various classes of  $C_{60}$  derivatized  $\pi$ -conjugated polymers<sup>12</sup> and oligomers<sup>13</sup> have been synthesized in view of their potential use as active material in organic photovoltaic devices. This approach has been initially considered in the case of poly(thiophenes) functionalized with  $C_{60}$  groups. These polymers have been the subject of a recent review by Cravino and Sariciftici who proposed the term “double cable” polymer to describe this class of ambipolar materials.<sup>12</sup> However, further consideration of this concept in the light of the work carried out on the parent oligomeric systems suggests that the term double cable might not be fully appropriate. By analogy with electrical circuits, a “double cable” system is expected to transport positive and negative charges through two independent “wires”. In this context, a “double cable” polymer should involve two isolated  $\pi$ -conjugated chains with electronic properties specifically tailored for holes and electrons transport respectively (Scheme 1a). Such a concept is exemplified by a solar cell based on a blend of the donor MEHPPV and the acceptor cyanoviny-PPV reported in 1995 by Halls *et al.*<sup>14</sup> Based on the well-known important intra-chain contribution to the overall conduction process in  $\pi$ -conjugated polymers (as illustrated by the concept of molecular wire), a blend of p-type and n-type conjugated polymers can be indeed considered as a double cable system (Scheme 1a). However,

it should be kept in mind that even for polymers with an extended effective conjugation length, the macroscopic conductivity always implies an important intermolecular charge-hopping contribution.

In the case of a molecular material based on short-chain  $\pi$ -conjugated oligomers attached onto  $C_{60}$ , the intra-chain contribution to hole transport tends to vanish as chain length decreases while intermolecular charge-hopping becomes the dominant mechanism (Scheme 1b). Similarly, electron transport, which was ensured by an n-type polymer in the previous case (1a), now proceeds by charge hopping between  $C_{60}$  groups. Examination of the charge transport in  $C_{60}$ -derivatized conjugated polymers in the light of the two above limiting situations shows that such polymers represent a hybrid situation where hole transport involves a substantial intra-chain contribution along the  $\pi$ -conjugated backbone while electron transport exclusively occurs by charge-hopping between the  $C_{60}$  groups (Scheme 1c) and the term “double cable” polymers seems inappropriate for such a hybrid conduction mechanism. On the other hand, when considered at the molecular level, a  $C_{60}$ -derivatized oligomer can be viewed as a molecular hetero-junction. Although this picture is not appropriate in solid state devices since photo-induced electron transfer can involve conjugated chains and  $C_{60}$  groups of different molecules, at the molecular level it represents an interesting view for the analysis and structural optimization of the photo-induced charge transfer process. Furthermore, as discussed below, molecular devices will



Scheme 1

probably represent an important area for future research on organic photovoltaics.

### 3 C<sub>60</sub>-derivatized $\pi$ -conjugated polymers

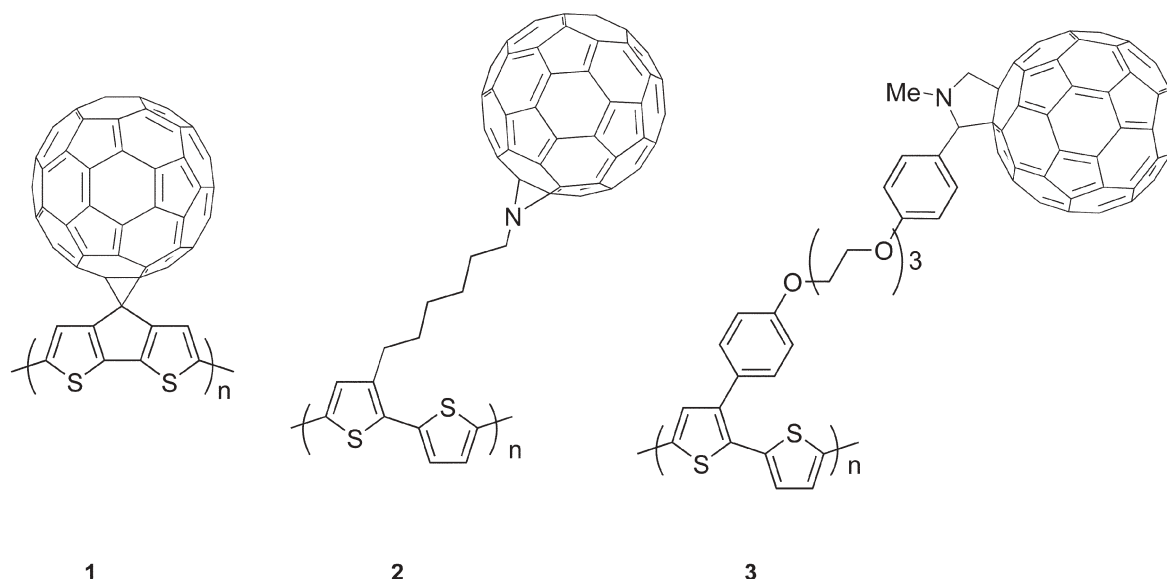
The most efficient solar cells based on organic bulk heterojunctions have been realized with poly-disperse  $\pi$ -conjugated polymers such as PPV or PAT derivatives.<sup>9</sup> In fact polymers present some important advantages. First, soluble conjugated polymers have in general better film-forming properties than oligomers which is important for device fabrication and for the mechanical properties of the final solar cell. Furthermore, polymers are generally prepared by more straightforward synthetic methods than the tedious multi-step syntheses required for the preparation of well-defined  $\pi$ -conjugated oligomers. Finally, because of the decrease of the HOMO–LUMO gap with chain extension, conjugated polymers should in principle present the lowest limit of the band gap and hence the optimum of the absorption of the solar emission spectrum for a conjugated system of given chemical constitution. In spite of these potential advantages, the number of examples of C<sub>60</sub>-derivatized  $\pi$ -conjugated polymers synthesized until now remains considerably smaller than that of molecular systems based on  $\pi$ -conjugated oligomers and C<sub>60</sub>.

Poly(thiophene), which combines the potential advantages of a better photo-stability and smaller band gap than *e.g.* PPV derivatives, has been the most widely used substrate for the synthesis of C<sub>60</sub>-derivatized conjugated polymers. Covalent fixation of C<sub>60</sub> onto a polythiophene structure was initially investigated by Sannicolò and coworkers.<sup>15</sup> Cyclopentabithiophene was converted into a stable diazo derivative by a diazo transfer reaction and the resulting compound was reacted with C<sub>60</sub> to give the methanofullerene **1** in 50% yield. The cyclic voltammogram of compound **1** recorded in a toluene–acetonitrile mixture showed three reversible one-electron reduction processes typical of C<sub>60</sub>. Attempts to electropolymerize the cyclopentadithiophene group in that medium remained unsuccessful but some electropolymerization could be observed in

chlorobenzene. Although the CV of the resulting material exhibited cathodic waves associated with the reduction of the C<sub>60</sub> group, the redox system corresponding to the p-doping/undoping process of the polythiophene backbone was observed at a more positive potential than for the parent poly(cyclopentabithiophene). This result was the consequence of a combination of the electronic and steric effects of the attached fullerene and of a limited degree of polymerization caused by the low solubility of the precursor. The optical spectrum of the undoped polymer showed an absorption maximum at 440 nm. The 115 nm blue shift of  $\lambda_{\text{max}}$  compared to that of the electropolymerized unsubstituted poly(cyclopentabithiophene) confirmed the short effective conjugation of the PT backbone due probably to the fact that electropolymerization was limited to the formation of short chain oligomers.

Ferraris and co-workers have described the synthesis of a bithiophene with a C<sub>60</sub> group attached at an internal  $\beta$ -position of one thiophene ring *via* an alkyl spacer (**2**).<sup>16</sup> In addition to reducing steric interactions, the alkyl spacer contributes to improve the solubility of the precursor. Electropolymerization was achieved by application of repetitive potential scans to a dichloromethane solution of **2**. The CV of the resulting polymer showed a broad redox system with an anodic peak at 0.74 V *vs.* Ag/Ag<sup>+</sup> corresponding to the oxidation of the PT backbone. The negative potential region exhibited a series of reversible reduction peaks at –0.58, –1.03, –1.47, –1.87 associated with the successive reduction of the attached C<sub>60</sub>, while the most negative reduction wave observed at –2.25 V was attributed to the n-doping of the PT backbone. The neutral polymer shows an absorption maximum at 480 nm. The similarity of this value with that of poly(bithiophene) confirms the neutralization of the electronic and steric effects of the attached C<sub>60</sub> on the effective conjugation length of the conjugated polymer backbone.<sup>16</sup>

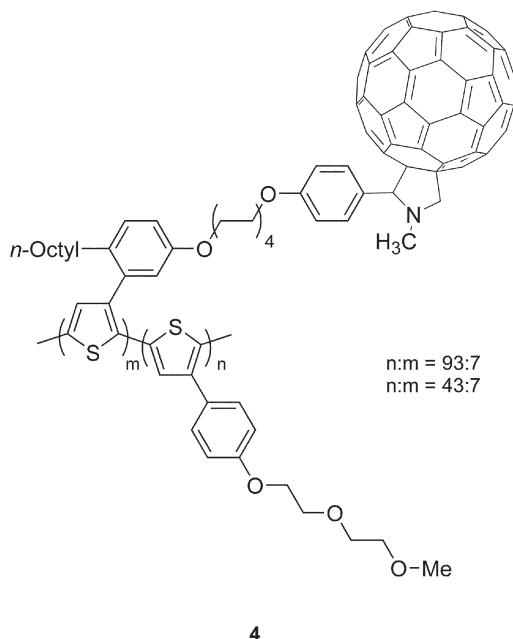
An electrogenerated polymer derived from a bithiophene–fulleropyrrolidine dyad in which the C<sub>60</sub> group was connected to the  $\pi$ -conjugated backbone chain *via* a phenyl



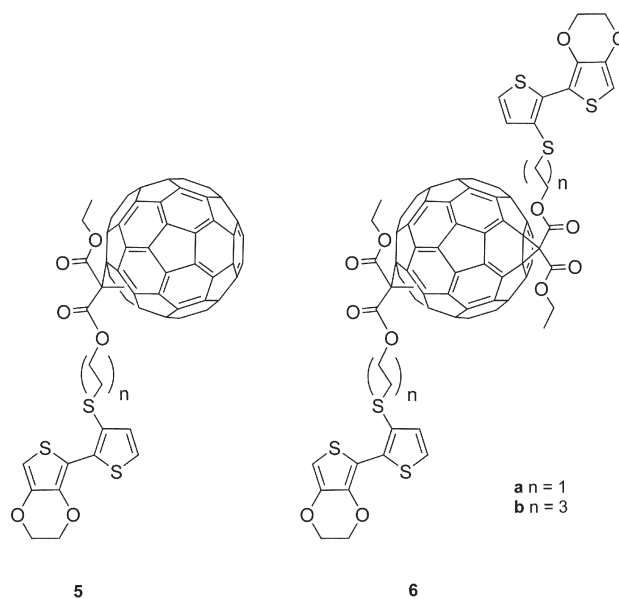


polyether linker (**3**) has been reported by Cravino *et al.*<sup>17</sup> Potentiodynamic electropolymerization was successfully achieved in dichloromethane or toluene–acetonitrile mixtures. The cyclic voltammogram of the resulting polymer showed a broad redox system centered around 0.75 V *vs.* Ag/AgCl corresponding to the p-doping/undoping process of the polythiophene backbone while the negative potential region exhibited successive reduction waves associated with the formation of the C<sub>60</sub> anionic states. The polymer film did not exhibit any photoluminescence and the photo-induced absorption spectra in the Vis-NIR after excitation at 476 nm showed two transitions around 1.40 and 0.60 eV characteristic of the PT polaronic state. The square-root intensity dependence of these two transitions was interpreted by an absence of geminate hole–electron recombination, suggesting possible migration of charge carriers in the material. ESR experiments performed under light excitation confirmed the photo-induced formation of the poly(thiophene) polaronic state and C<sub>60</sub> radical anion. These results thus provided clear evidence for a long-lived and mobile charge-separated state in this electro-generated polymer.<sup>12,17</sup>

Zhang *et al.* have synthesized soluble copolymers by chemical co-polymerization of a C<sub>60</sub>-derivatized monomer with another thiophenic monomer unit bearing a solubilizing polyether chain (**4**). The use of different ratios of the two monomers led, after work-up, to two soluble copolymers containing 7 and 14 mol% of the fullerene-derivatized monomer.<sup>18</sup> These copolymers were then used for the fabrication of photodiodes. The photodiode made from the copolymer with the largest C<sub>60</sub> content showed an incident photon conversion efficiency (IPCE) *ca.* twice larger than that prepared from the other copolymer. A power conversion efficiency of 0.60% was obtained under monochromatic irradiation at  $\lambda = 505$  nm at low irradiation intensity (0.10 mW cm<sup>-2</sup>).<sup>18</sup>



We have described another series of C<sub>60</sub>-derivatized polythiophenes prepared by electropolymerization of precursors **5** and **6** in which polymerizable groups are attached onto C<sub>60</sub> with alkyl spacers of variable length.<sup>19</sup> The polymerizable groups in the precursors of these polymers are based on the association of the strong electron donor 3,4-ethylenedioxythiophene with a 3-alkylsulfanylthiophene. As shown already for various classes of functional poly(thiophenes), this type of tailored precursor structure allows the achievement of an efficient electropolymerization at low potential.

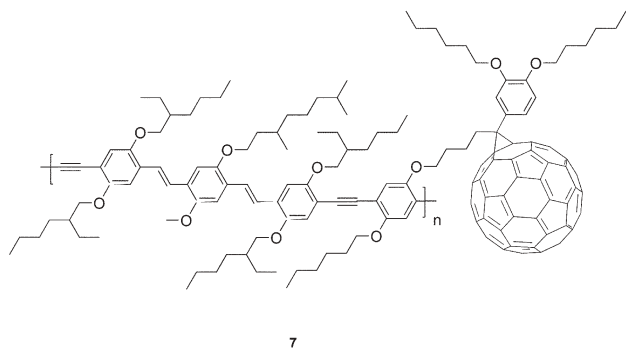


Furthermore, in addition to a mild and efficient approach for the functionalization of thiophene *via* the facile deprotection of a thiolate function, the formation of a sulfide group contributes to a decrease of electropolymerization potential of compounds **5** and **6** to values lower than one volt *vs.* SCE. A comparative analysis of the electrochemical and optical properties of the polymers derived from precursors **5** and **6** has shown that a two-site precursor (**6**) leads to a more efficient electropolymerization process and to a more stable and more porous polymer.<sup>19</sup>

Preliminary tests of the photo-electrochemical response of a film of poly(**6b**) on a platinum electrode showed that the photo-generated current is *ca.* three times larger than that obtained under the same conditions with a polymer based on the same type of precursor but devoid of attached C<sub>60</sub>. Although this result underlines the potentialities of this new class of polymers for photovoltaic conversion, the synthesis of processable analogs of these materials is needed in order to evaluate their performances in real solid-state devices.

A first example of a solar cell based on a C<sub>60</sub>-derivatized PPV type polymer of hybrid structure was reported by Janssen and coworkers. The C<sub>60</sub> group was introduced by means of a reaction between a diiodobenzene bearing the attached C<sub>60</sub> and oligophenylenevinyls with terminal alkynes. This synthetic approach leads to a polymer with a theoretical ratio of one C<sub>60</sub> group for four benzene rings, **7**.<sup>20</sup> Quenching of the photoluminescence of the conjugated backbone was observed both in solution and in the solid state. This latter process was attributed to a photo-induced electron transfer.

A photovoltaic cell prepared using a spin-coated film of **7** gave under white light irradiation ( $100 \text{ mW cm}^{-2}$ ) a short-circuit current of  $0.42 \text{ mA cm}^{-2}$ , an open-circuit voltage of  $0.83 \text{ V}$  and a fill-factor of  $0.29$ .<sup>20</sup>



To the best of our knowledge, these performances are the highest reported so far for a cell based on a single component  $\text{C}_{60}$ - $\pi$ -conjugated system. Although these characteristics are still markedly inferior to those of the cells based on mixtures of the two individual components, these results clearly confirm the potentialities of  $\text{C}_{60}$ -derivatized conjugated polymers for the realization of organic solar cells.

#### 4 $\text{C}_{60}$ -derivatized conjugated oligomers

While initial work on single component systems for photovoltaic conversion has mainly concerned polymers functionalized with fullerene  $\text{C}_{60}$ , recent years have witnessed a strong intensification of research aiming at the synthesis of  $\text{C}_{60}$ -derivatized  $\pi$ -conjugated oligomers.<sup>13</sup> In fact, oligomers present several inherent advantages. First, because of their well-defined chemical structure,  $\text{C}_{60}$ -derivatized  $\pi$ -conjugated oligomers make it possible to investigate structure-properties relationships on homologous series of conjugated structure of increasing chain length and thus decreasing HOMO-LUMO gap. This allows in particular detailed investigations on the effects of chain extension on the elemental photophysical processes of light absorption, photo-induced energy and/or electron transfer and eventually on the final output performances of the derived solar cells. Another important point is that working with well-defined  $\pi$ -conjugated oligomers should allow the avoidance of the statistical distribution of chain lengths inherent to conjugated polymers and hence make it possible to work on systems in which all donor conjugated segments possess in principle the same effective conjugation length and hence energy gap and oxidation potential. These latter points can be particularly important as far as parameters such as interfacial field, charge separation and recombination, open-circuit voltage and hole transport are concerned.

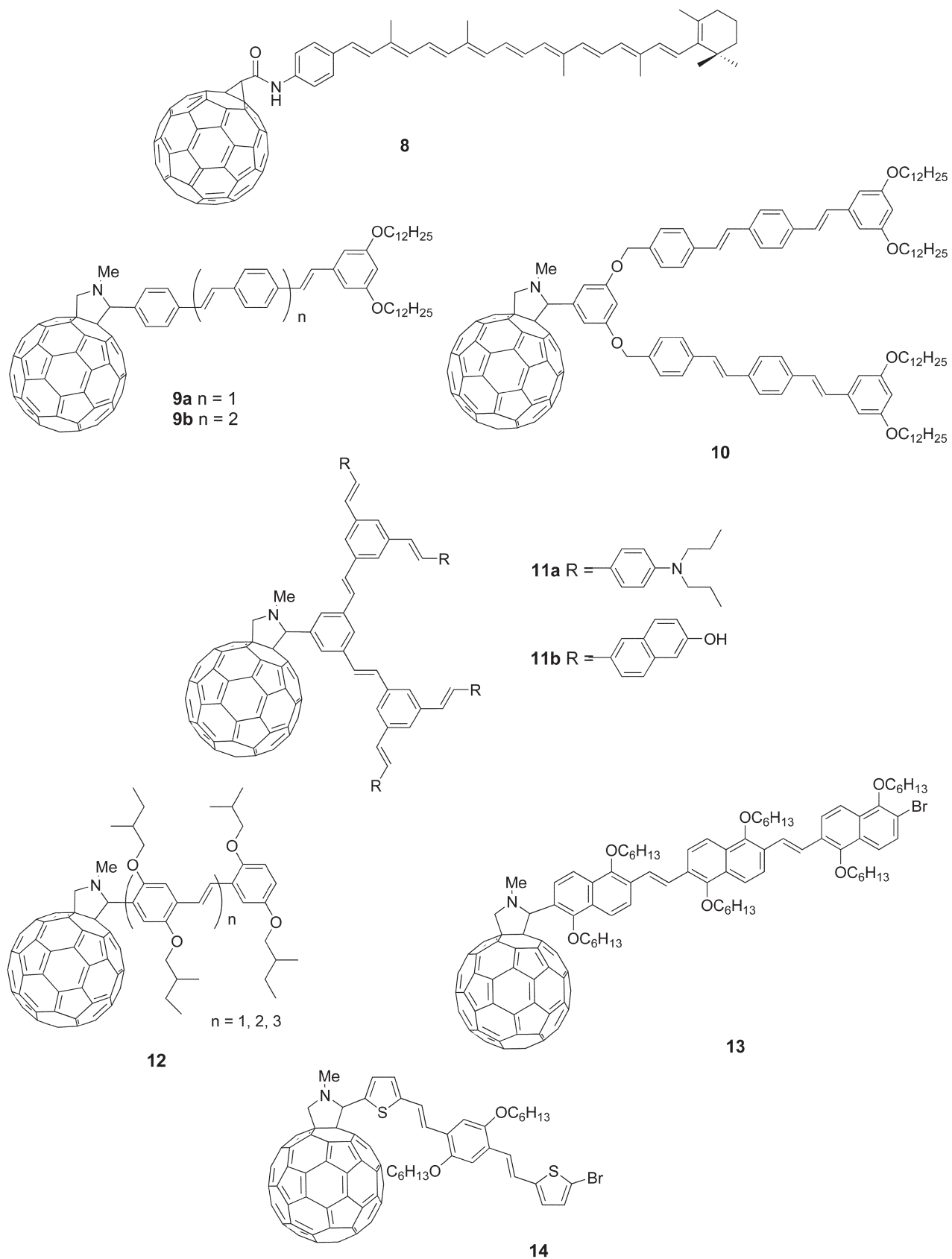
The considerable development of the chemistry of fullerenes during the past decade has given rise to the synthesis of a huge number of dyads involving donor groups covalently attached onto  $\text{C}_{60}$ .<sup>11</sup> Concerning the more specific area of photoactive systems, porphyrin and chlorophyll groups have been most frequently used as electron donors in artificial photosynthetic models,<sup>21</sup> whereas molecular systems for photovoltaic

conversion generally resort to  $\text{C}_{60}$ -derivatized linearly  $\pi$ -conjugated systems.

A first example of a  $\text{C}_{60}$ -derivatized linear  $\pi$ -conjugated system was reported in 1995 by Imahori *et al.* who analyzed the photochemical properties of a carotenoid-linked  $\text{C}_{60}$  **8**.<sup>22</sup> In 1999, Nierengarten *et al.* reported the synthesis of a full-eropyrrolidine derivative bearing a short chain oligophenylenevinylene (OPV) **9a**.<sup>23</sup> This compound can be considered as the first example of a molecular hetero-junction specifically designed for photovoltaic conversion. The electronic absorption spectrum of the molecule corresponded to the sum of the spectra of the two components, indicating an absence of ground-state interaction between the  $\pi$ -conjugated chain and the attached  $\text{C}_{60}$ . However, a strong quenching of the luminescence of the OPV was observed. A simple device was assembled by spin-casting a film of **9a** from a chloroform solution on an indium-tin oxide coated glass electrode and the device was completed by a vacuum evaporated aluminium electrode. The device delivered a short circuit current density ( $J_{\text{sc}}$ ) of  $10 \mu\text{A cm}^{-2}$  and an open circuit voltage ( $V_{\text{oc}}$ ) of  $0.46 \text{ V}$  under monochromatic irradiation ( $400 \text{ nm}$ ,  $12 \text{ mW cm}^{-2}$ ). Increasing the length of the OPV from three to four units (**9b**) did not significantly increase the conversion efficiency. Both devices did not show any rectification behaviour. The limited efficiency of these devices has been attributed to the competition between energy transfer and electron transfer.<sup>24</sup>

More detailed information has been gained by synthesizing compound **10** in which two OPV chains are attached to  $\text{C}_{60}$ .<sup>25</sup> Again the ground state UV-vis spectrum coincided with the sum of the spectra of the OPV and  $\text{C}_{60}$  building blocks. Upon selective excitation of the  $\text{C}_{60}$  fragment the typical fluorescence and triplet-triplet transient absorption spectra were observed. On the other hand, selective excitation of the OPV chain did not permit observation of its specific fluorescence whereas that of  $\text{C}_{60}$  was detected. The excitation spectrum of the whole molecule taken at the emission of  $\text{C}_{60}$  matches the total absorption spectrum including the spectral region corresponding to the OPV absorption. These results have been attributed to a quantitative singlet-singlet energy transfer from the OPV to the  $\text{C}_{60}$  unit.<sup>25</sup> More recently, the analysis of the photophysical properties of compounds **11a** and **11b** in which conjugated dendrons are attached to a  $\text{C}_{60}$  group led to the conclusion that energy transfer competes with an activated electron transfer.<sup>26</sup>

Janssen and coworkers have carried out detailed investigations on the chain length dependence of the photophysical properties of a homologous series of OPV- $\text{C}_{60}$  containing one to four phenyl rings (**12**).<sup>27</sup> Photo-excitation of the OPV moiety in apolar solvents led to a fast singlet energy transfer from the OPV toward the  $\text{C}_{60}$  moiety. This fast energy transfer is followed by a nearly quantitative inter-system crossing to the  $\text{C}_{60}$  triplet state. In contrast, in polar solvents, photo-excitation of the dyads resulted in electron transfer from the OPV to the  $\text{C}_{60}$  group with formation of a charge-separated state when the conjugation length of the OPV exceeds one PV unit. These conclusions were supported by studies performed in the solid state on solution processed thin films. Long-lived charge-separated states were observed for compounds containing three and four OPV units. A photovoltaic device fabricated



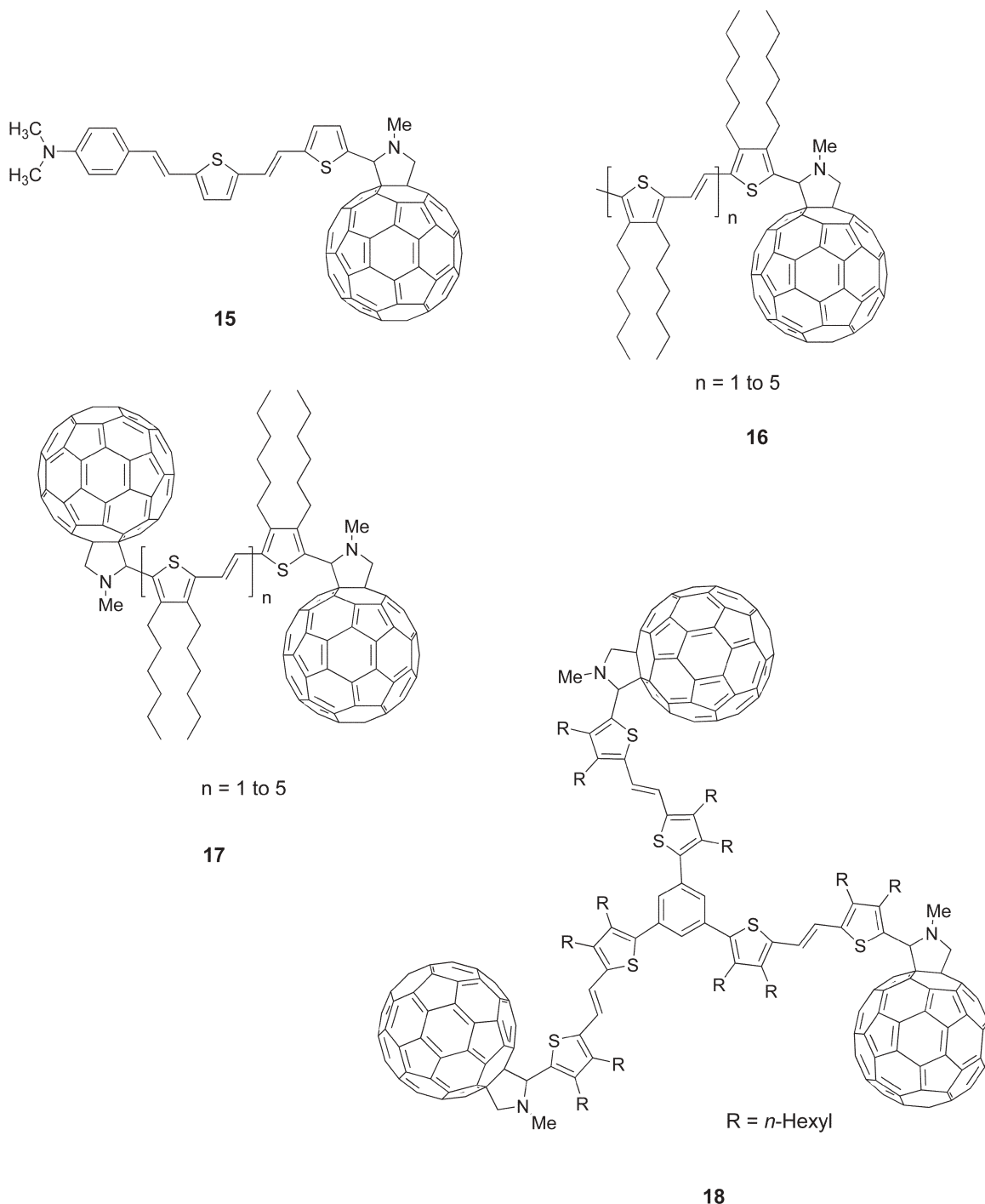
using the longest system (four PV units) gave encouraging results, namely a short-circuit current density of  $235 \mu\text{A cm}^{-2}$  and a  $V_{\text{oc}}$  of 0.65 V under  $65 \text{ mW cm}^{-2}$  white-light irradiation.<sup>27</sup>

Further examples of competition between intra-molecular energy and electron transfer have been provided by the analysis of the photophysical properties of oligo(naphthylene-vinylene)-fullerene dyads (**13**).<sup>28</sup>

A dyad involving the hybrid thiophene-based conjugated system **14** embedded in an asymmetric metal contact gave an

external quantum efficiency close to 10% under monochromatic irradiation at the maximum absorption of the molecule.<sup>28</sup>

On the basis of our intensive previous studies on oligothienylenevinylenes (*n*TVs), we have recently synthesized series of linear or branched *n*TVs bearing one to three terminal  $\text{C}_{60}$  groups (**15–18**).<sup>29,30</sup> The cyclic voltammograms of all the compounds exhibited the multiple redox systems typical of the electrochemical signature of the *n*TV chain in the positive potential region and of the anion radical and dianion of  $\text{C}_{60}$  in





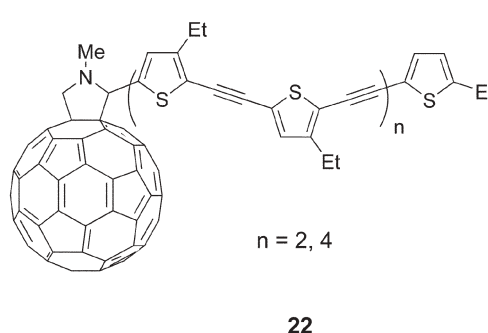
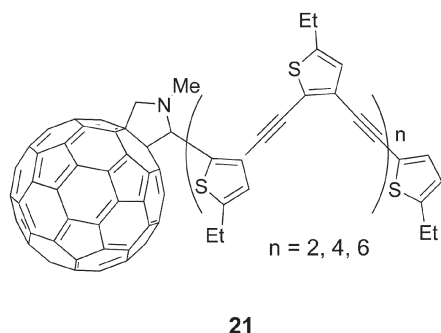
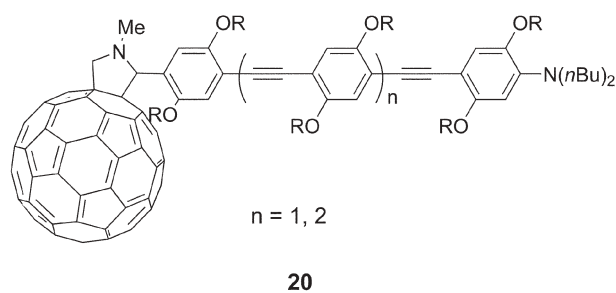
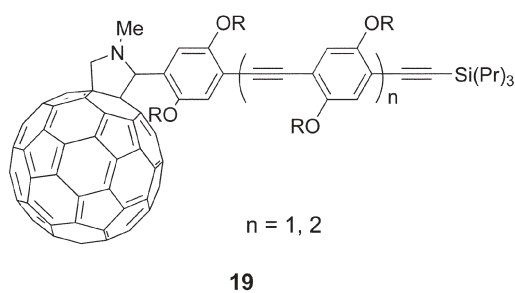
the negative potential region. In particular a change from a one-electron to a two-electron first oxidation process was observed as the chain length of the *n*TV reaches 8 TV units, while the intensity of the redox systems associated with the reduction of C<sub>60</sub> increased in proportion to the number of attached C<sub>60</sub> groups.<sup>30</sup> The photophysical properties of a homologous series of *n*TVs systems with *n* = 2, 3, 4, 6, 8 and 12 have been investigated in the presence of *N*-methylfulleropyrrolidine (MP-C<sub>60</sub>) as acceptor in apolar and polar solvents. Whereas the shorter oligomers (*n* = 2 and 3) fluoresce, the singlet excited-state lifetime of the longer oligomers is extremely short because of a fast thermal decay. Photo-induced absorption spectroscopy demonstrated that the *n*TV triplet state can be populated indirectly *via* intermolecular triplet energy transfer using photo-excited MP-C<sub>60</sub> as sensitizer. In the more polar *o*-dichlorobenzene solvent the MP-C<sub>60</sub> (T<sub>1</sub>) state acts also as an oxidizing agent allowing the formation of a metastable radical ion pair (*n*TV<sup>+</sup> + MP-C<sub>60</sub><sup>-</sup>). In the case of the covalently attached systems **16** (*n* = 2 to 4), photo-excitation of the *n*TV chain leads to an ultra fast singlet energy transfer to MP-C<sub>60</sub> followed by an intra-molecular electron transfer. The intra-molecularly charge-separated state is the lowest energy excited state in polar medium. In toluene, the charge-separated state is formed only for *n* > 2 and competes with fluorescence and inter-system crossing to the MP-C<sub>60</sub> (T<sub>1</sub>) state.<sup>31</sup>

Hybrid oligomeric structures incorporating acetylenic linkages such as phenyleneethynylenes and thienyleneethynylenes have also been attached onto C<sub>60</sub>. Gu *et al.* have reported the synthesis of fullerene-oligophenyleneethynylenes with terminal tripropylsilyl or dibutylamino groups (**19**, **20**).<sup>32</sup> For all compounds, the UV-vis spectrum exhibits the spectral signature of the two individual building blocks, indicating an

absence of significant ground-state interactions. Conversely the quenching of the luminescence of the  $\pi$ -conjugated chain indicated the occurrence of intra-molecular photo-induced processes. In addition to the typical signature of the reduced C<sub>60</sub>, cyclic voltammetry showed that, as expected, the compounds containing dibutylamino groups present lower oxidation potentials. The photovoltaic properties of the compounds were tested under monochromatic illumination on devices made from spin-coated films sandwiched between ITO and aluminium electrodes. The best results were obtained with shorter chain lengths while compounds with dialkylaniline end groups gave efficiencies higher by *ca.* one order of magnitude with values in the range of 0.02% under 1 mW cm<sup>-2</sup> monochromatic irradiation (400 nm).<sup>32</sup>

Otsubo and coworkers have synthesized C<sub>60</sub>-derivatized oligothiopheneethynylene dyads with two different modes of attachment of the thiophene ring onto the fulleropyrrolidine group **21**, **22**.<sup>33</sup> The analysis of the fluorescence properties of these compounds in toluene revealed two distinct photo-induced intra-molecular interactions between the oligomer and C<sub>60</sub>. Whereas through-bond interactions were observed for the 2,5-thienylene system (**22**), through-space interactions were detected for the 2,3-thienylene based system (**21**).<sup>33</sup>

Oligothiophenes (*n*Ts) have been widely used as a  $\pi$ -conjugated donor system in C<sub>60</sub> dyads. The covalent fixation of *n*Ts onto C<sub>60</sub> was initially investigated by Effenberger *et al.*<sup>34</sup> Attempts to prepare thienyl-fullerenes by addition of thiophene and oligothiophenes as organolithium reagents to C<sub>60</sub> gave very low yields of the target molecules. Although the use of 2,3-bis(bromomethyl)thiophene as a source of *in situ* generated *o*-quinodimethane gave the mono-adduct in 42% yield, all attempts to extend this approach to the synthesis of longer *n*T-C<sub>60</sub> dyads failed because of the instability of the

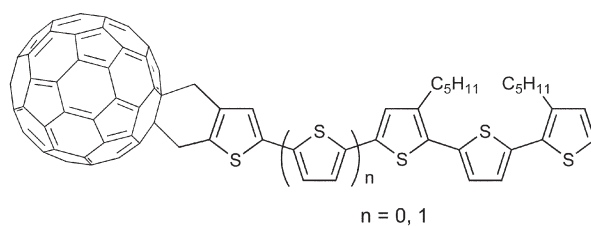


corresponding 2,3-bis(bromomethyl) derivatives. The target compounds (**23**) were finally obtained using sulfones as precursors for the generation of the *o*-quinodimethane intermediates.<sup>34</sup>

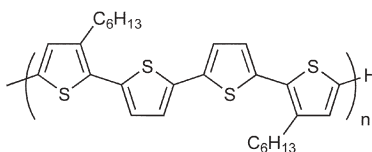
Otsubo and coworkers have synthesized a series of *n*Ts- $C_{60}$  systems involving four, eight and twelve thiophene rings (**24**).<sup>35</sup> The analysis of the luminescence properties of these systems revealed a strong quenching of the fluorescence of the *n*T chain. Detailed investigations of the effect of the solvent polarity on the photophysical properties of the shortest system ( $n = 1$ ) have shown that charge separation, which is not observed in a non polar solvent such as toluene, occurs at a

rate on the order of  $10^{10} \text{ s}^{-1}$  in polar solvents such as tetrahydrofuran or benzonitrile and with a quantum yield close to unity.<sup>35</sup>

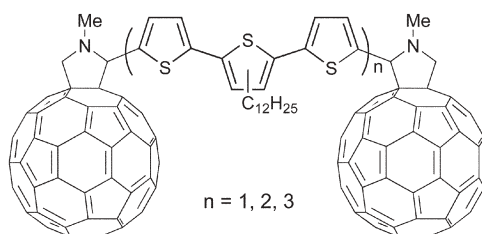
Janssen and coworkers have synthesized a series of fullerene-oligothiophene-fullerene ( $C_{60}$ -*n*Ts- $C_{60}$ ) triads containing 3, 6 and 9 thiophene units (**25**).<sup>36</sup> The photophysical properties of these compounds have been investigated by photo-induced absorption and fluorescence spectroscopies in solution and in the solid-state and the results were compared to those obtained with a binary mixture of *n*Ts and *N*-methylfulleropyrrolidine. A major goal of the work was to investigate whether the large difference in forward and



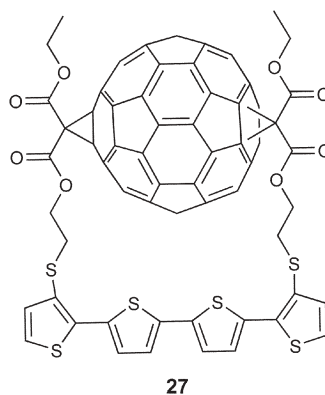
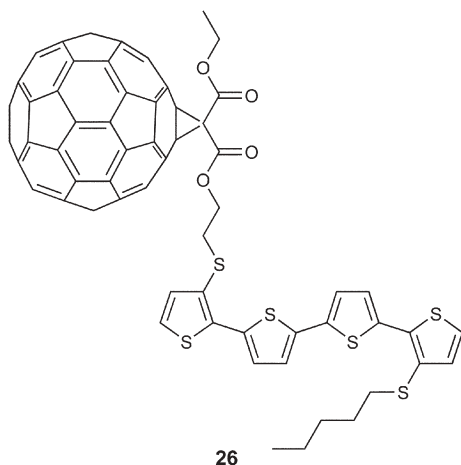
**23**



**24**



**25**



backward electron-transfer rates observed in conjugated polymers/fullerene composites was an intrinsic property of the molecules involved or a material property. As in previous cases, a strong quenching of the fluorescence of the oligothiophene chain was observed.<sup>36</sup> In apolar solvents, photo-excitation of the triads results in a singlet energy transfer reaction to the fullerene moiety. In polar solvents, intramolecular photo-induced charge separation electron transfer occurs for *n*Ts chains containing 6 and 9 thiophene units and to a lesser extent for the shortest system. In the solid films, the lifetime of the charge-separated state extends into the millisecond time domain, suggesting an intermolecular migration of the photo-generated charges.<sup>36</sup>

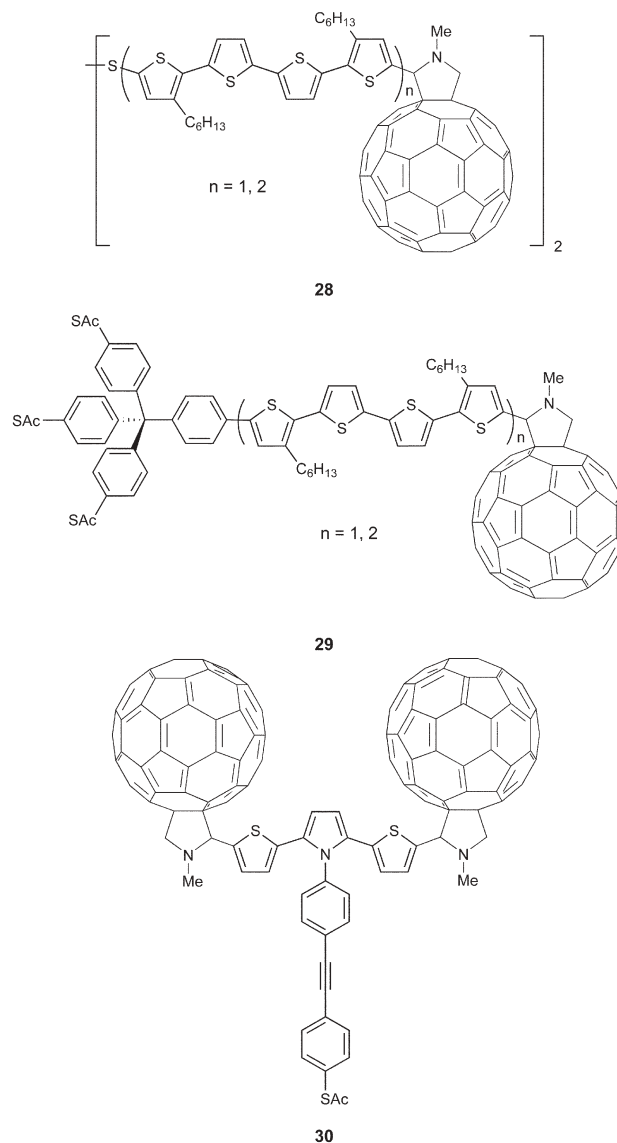
In order to investigate the influence of the effects of the relative orientation of the C<sub>60</sub> and conjugated chains, we have synthesized quaterthiophene-C<sub>60</sub> dyads in which the conjugated chain is singly (**26**) or doubly (**27**) connected to the C<sub>60</sub> moiety.<sup>37</sup> The analysis of the photophysical properties of these systems carried out by Janssen and coworkers has shown that in both cases a photo-induced electron transfer occurred in a polar solvent such as chlorobenzene. In the non polar toluene, charge transfer occurs *via* an indirect mechanism involving first a singlet-singlet energy transfer. The double fixation of the quaterthiophene chain was found to increase the rate constant for photo-induced electron transfer by *ca.* one order of magnitude. However it was also found that the double fixation of the quaterthiophene chain also enhances the rate for charge recombination.<sup>37</sup>

## 5 Self-assembled monolayers of $\pi$ -conjugated systems-C<sub>60</sub> adducts

The fixation of C<sub>60</sub>-derivatized  $\pi$ -conjugated systems onto metal surfaces as self-assembled monolayers (SAMs) represents one of the most recent developments of organic photovoltaics. Besides their fundamental interest, such SAMs could pave the way towards nanoscale photovoltaic devices. Hirayama *et al.* have reported the synthesis of quater- and octi-thiophene linked to a gold surface with a disulfide anchoring group (**28**).<sup>38</sup> The CV of the SAM on a gold surface exhibits a first reduction wave typical for C<sub>60</sub>. Photo-electrochemical experiments were carried out on a monolayer of the *n* = 2 compound immersed in a solution containing methylviologen as electron carrier. A photocurrent of several hundreds of nA cm<sup>-2</sup> was observed under 440 nm monochromatic irradiation at 22 mW cm<sup>-2</sup> under slightly negative bias. The same group has developed another class of SAMs in which the anchoring onto the surface is ensured by a tripodal group (**29**).<sup>39</sup> This mode of fixation leads to a more dense surface coverage than the previous single-point attachment. Under monochromatic light irradiation (0.65 mW cm<sup>-2</sup> at 400 nm) the photo-electrode delivered a current density approaching 1  $\mu$ A cm<sup>-2</sup> when the photo-electrode was biased at -0.10 V *vs.* Ag/AgCl in the presence of methyl viologen as electron carrier.<sup>39</sup>

Very recently, Jen and coworkers have reported the synthesis of a SAM in which the fixation of the anchoring site onto the nitrogen atom of the median pyrrole group (**30**) allows the conjugated chain to adopt an orientation parallel to

the surface.<sup>40</sup> Photo-electrochemical experiments under 400 nm irradiation with 0.85 mW cm<sup>-2</sup> and a bias voltage of -0.10 V *vs.* Ag/AgCl, showed that the SAM delivered a current density of 3200 nA cm<sup>-2</sup>. This value, considerably larger than those reported for related systems, was attributed to the possible orientation of the conjugated system perpendicularly to the direction of the incident light.<sup>40</sup>



## Conclusion

Adducts of  $\pi$ -conjugated systems and fullerene C<sub>60</sub> have generated a considerable research effort during the past decade. Initially developed as model systems for artificial photosynthesis, the interest in these compounds has received a further impetus with the rapid emergence of organic solar cells based on interpenetrated networks of conjugated polymers and soluble C<sub>60</sub> derivatives.

Initially viewed as a possible approach for a molecular control of the interactions between the  $\pi$ -conjugated system and the C<sub>60</sub> group in bulk hetero-junction solar cells,

C<sub>60</sub>-derivatized  $\pi$ -conjugated systems have progressively generated interest on their own, thus giving rise to new research areas.

Various classes of C<sub>60</sub>-derivatized conjugated polymers have been synthesized with the aim of optimizing bulk hetero-junction solar cells and in particular controlling the structure and properties of the interface of the molecular hetero-junction. However, and despite some encouraging results, many parameters still need to be optimized before such derivatized polymers can provide a viable alternative to the well established two-component cells. In fact solutions to problems like for example low solubility, low molecular weight and polydispersity will require considerable further effort with a probably excessive cost in terms of synthetic investment. In this context it could be most advantageous to improve the two-component systems by other strategies such as the realization of nano-structured materials by means of non-covalent interactions between tailored  $\pi$ -conjugated systems or C<sub>60</sub> derivatives specifically designed for molecular recognition and self-organization by means of non covalent interactions. The post polymerization functionalization of conjugated polymers also represents another interesting possibility which remains so far unexplored.

However a major problem rather poorly considered so far lies in the major contradiction represented by the association of a C<sub>60</sub> phase which can be more or less viewed as a sphere percolation system able to ensure an isotropic electron transport, with linear  $\pi$ -conjugated systems in which efficient hole transport requires strong  $\pi$ -stacking interactions in which hole transport occurs preferentially in the  $\pi$ -stacking direction. This basic problem which is also posed by the replacement of the liquid electrolyte by a solid-state hole transport material in a dye-sensitized TiO<sub>2</sub>-based solar cell shows that substantial synthetic chemistry effort should be invested in the design and synthesis of  $\pi$ -conjugated systems able to ensure an efficient 3D hole transport; in fact such a project is now under development in our group.

Initially developed as a branch of the huge activity related to the chemistry of C<sub>60</sub> adducts, molecular hetero-junctions based on adducts of C<sub>60</sub> and  $\pi$ -conjugated oligomers have progressively emerged as a new research area with in particular the realization of photo-electrochemical systems capable of generating appreciable photo-currents.

From a fundamental viewpoint molecular hetero-junctions based on well-defined  $\pi$ -conjugated oligomers remain ideal model systems for the investigation of the relationships between structural parameters such as the ratio, distance, relative orientation and nature of the link between the donor and the acceptor, and the multiple elemental processes involved in photon-electron conversion *i.e.* absorption, photo-induced energy and/or electron transfer, and charge separation.

On the other hand, these molecular hetero-junctions have also led to some first prototypes of molecular photovoltaic devices and it seems likely that such molecular architectures will acquire a growing importance in the expanding field of nanosciences and molecular electronics.

As for the parent polymer-based systems, progress in this emerging field lies in the development of an intensive research

effort of creative synthetic chemistry inserted in a broad interdisciplinary perspective.

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