ACCOUNTS
of chemical research

Molecular Bulk Heterojunctions: An Emerging Approach to Organic Solar Cells

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RECEIVED ON FEBRUARY 2, 2009

CONSPECTUS

The predicted exhaustion of fossil energy resources and the pressure of environmental constraints are stimulating an intensification of research on renewable energy sources, in particular, on the photovoltaic conversion of solar energy. In this context, organic solar cells are attracting increasing interest that is motivated by the possibility of fabricating large-area, lightweight, and flexible devices using simple techniques with low environmental impact.

Organic solar cells are based on a heterojunction resulting from the contact of a donor (D) and an acceptor (A) material. Absorption of solar photons creates excitons, Coulombically bound electron−hole pairs, which diffuse to the D/A interface, where they are dissociated into free holes and electrons by the electric field. D/A heterojunctions can be created with two types of architectures, namely, bilayer heterojunction and bulk heterojunction (BHJ) solar cells. BHJ cells combine the advantages of easier fabrication and higher conversion efficiency due to the considerably extended D/A interface.

Until now, the development of BHJ solar cells has been essentially based on the use of soluble π-conjugated polymers as donor material. Intensive interdisciplinary research carried out in the past 10 years has led to an increase in the conversion efficiency of BHJ cells from 0.10 to more than 5.0%. These investigations have progressively established regioregular poly(3-hexylthiophene) (P3HT) as the standard donor material for BHJ solar cells, owing to a useful combination of optical and charge-transport properties. However, besides the limit imposed to the maximum conversion efficiency by its intrinsic electronic properties, P3HT and more generally polymers pose several problems related to the control of their structure, molecular weight, polydispersity, and purification. In this context, recent years have seen the emergence of an alternative approach based on the replacement of polydisperse polymers by soluble, conjugated single molecules as donor materials in BHJ cells. In fact, molecular donors present specific advantages in terms of structural definition, synthesis, and purification. In this Account, we present a brief survey of recent work in this nascent field of new single-molecule donors in organic solar cells.

Various series of three-dimensional donors built by the attachment of different kinds of conjugated branches on a central node, including silicon, twisted bithiophene, triphenylamine, and borondipyrromethene (BODIPY), are discussed in relation to the performances of the resulting solar cells. Furthermore, it is shown that the concept of a molecular donor with internal charge transfer leads at the same time to improved light-harvesting properties, red-shifted photoresponse, and a higher open-circuit voltage, resulting in a considerable increase of conversion efficiency, up to values now approaching 3%. These results show that soluble molecular donors can lead to BHJ cells that combine high conversion efficiency with the distinct advantages of working with single molecules, including structural definition, synthesis, purification, and reproducibility.
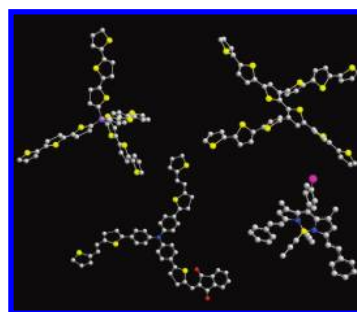
Introduction

The predictable exhaustion of fossil energy resources and the increasing pressure generated by environmental concerns and climate change have triggered an intensification of research on renewable energies and in particular on the photo- tovoltaic conversion of solar energy. Besides boosting the market for silicon solar cells, this context has also strongly contributed to arouse the interest of the scientific community in organic solar cells (OSCs). Thus, within a few years, the status of OSCs has evolved from a topic of purely

fundamental research to become a possible industrial contribution to the problem of photovoltaic energy conversion.

In solar cells based on inorganic semiconductors such as silicon, the absorbed photons lead to the direct creation of free charge carriers. In contrast, in organic semiconductors based on π-conjugated systems because of the low dielectric constant of these materials, light absorption leads to the creation of excitons, strongly Coulombically bound electron−hole pairs. These excitons must then be dissociated by an electric field of sufficient intensity. In organic heterojunctions formed by contacting a donor and an acceptor material, the driving force for exciton dissociation is provided by the energy offset between the molecular orbitals of the donor and acceptor. Exciton dissociation into free charge carriers thus represents a key process that imposes one of the major limitations to the power conversion efficiency of organic solar cells.

The fabrication of a bilayer heterojunction with an efficiency approaching 1% by Tang in 1986 was a milestone in the development of OSCs.[1] Although bilayer heterojunctions are still intensively investigated[2,3] and remain an invaluable tool for the evaluation of new active materials, their performances are limited by the short exciton diffusion length in organic materials (typically 10−20 nm). Since the exciton dissociation process is confined to the donor−acceptor interfacial zone, only excitons produced at a distance shorter than their diffusion length have a good probability to reach the interfacial zone and generate free charge carriers. Consequently, the exciton diffusion length limits the maximum thickness of the active layer and thus the maximum fraction of the incident light that the cell can absorb and convert into electricity.

An efficient way to bypass this obstacle consists of the realization of interpenetrated networks of the donor and acceptor materials. In such a bulk heterojunction (BHJ), the huge extension of the donor/acceptor contacting area between the donor and acceptor materials leads to a considerable increase of the number of excitons dissociated and hence of the conversion efficiency of the cell.[4] A major advantage of BHJ solar cells is that they can be fabricated by rather simple solution processes thus allowing the production of flexible, low-cost, and large-area solar cells. However, a key issue concerns the realization of appropriate phase segregation in order to create domains of donor and acceptor material of optimal dimensions consistent with the exciton diffusion length while ensuring the continuity of the transport of holes and electrons in their respective phase. In 1992, Sariciftci et al. demonstrated that photoexcitation of a mixture of a poly-(*p*-phenylene vinylene) derivative and C_{60} fullerene resulted in an ultrafast highly efficient photoinduced electron transfer.[5] Fur-

thermore, the long lifetime of the metastable charge-separated state associated with the delocalization of the positive and negative charges over the π-conjugated system and the fullerene group respectively allow both efficient charge transport and charge collection at the electrodes.[4]

Fullerenes and in particular soluble C_{60} derivatives such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) have been a key component for the development of BHJ solar cells.[6] Besides a LUMO level allowing efficient photoinduced charge transfer from the donor, the spherical geometry of C_{60} leads to isotropic electron transport through a 3D percolation system, which seems particularly appropriate for charge transport in disordered media. Since the first reports on solution-processed BHJ solar cells, soluble π-conjugated polymers have represented the exclusive class of donor materials owing to their interesting combination of optical, electrical, and mechanical properties and to their availability in sufficient quantities. The first prototypes of BHJ cells were based on polymers of the PPV series initially developed for light-emitting devices.[4] In recent years, these polymers have been supplanted by regioregular poly(3-hexylthiophene) P3HT, which presents the advantages of a lower band gap and higher hole mobility.[7−9] Within a relatively short period P3HT has become the archetype donor for BHJ cells and power conversion efficiencies of ~5% have been recently reported by several groups.[7−9]

Despite these remarkable results, P3HT poses a number of problems related to its synthesis, purification, and intrinsic electronic properties. The initial synthesis of regioregular P3HT involved rather complex procedures under cryogenic conditions.[10] While the Grignard metathesis method has greatly simplified the process, both methods lead to polymers with remnant terminal bromine atoms, which must be eliminated by appropriate chemical treatment.[11] The regioregularity, molecular weight, and polydispersity of P3HT have been shown to significantly affect the performances of BHJ solar cells.[12] In fact, we and others have observed that solar cells fabricated with P3HT samples of different commercial sources lead to devices showing considerable differences in performances, which seems to imply that the control of structural variables and purity is far from trivial.

Owing to a band gap of ~1.90 eV and a rather narrow absorption band (fwhm ≈ 150 nm), P3HT can absorb only a limited fraction of the solar photons (~30%). Furthermore, a relatively high-lying HOMO level sets the maximum cell voltage to 0.60−0.65 V and represents a potential cause of instability in atmospheric conditions. Finally, the achievement of conversion efficiencies of 4−5% requires application of a post-process thermal treatment to the PCBM−P3HT composite
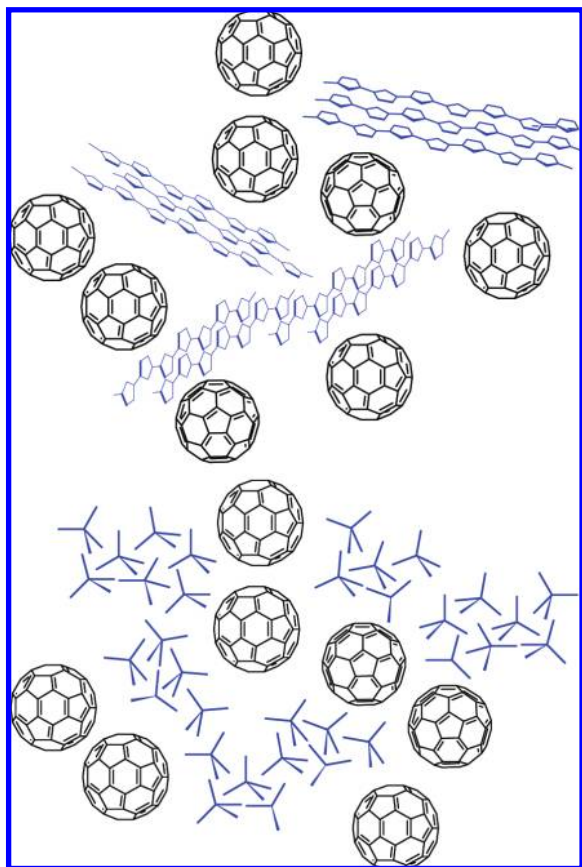
FIGURE 1. Schematic representation of BHJ based on polymers (top) and molecular donors (bottom).

material in order to improve the morphology of the bicontinuous phase and the crystallinity of P3HT.[13]

Because of their one-dimensionality, linearly π-conjugated systems such as poly(3-alkylthiophenes) present an anisotropic charge transport that is maximal in the stacking direction of the conjugated chains in the microcrystalline domains (Figure 1). Although this anisotropy is randomized by a large number of microdomains, it is not certain that one-dimensional π-conjugated systems represent the best molecular architecture to ensure 3D hole transport in BHJ cells.

A possible solution to these problems could consist in the replacement of π-conjugated polymers by soluble small conjugated molecules as donor material. Such an approach would present several potential advantages:

- A perfectly defined chemical structure erases the problems posed by the structural variability of polymers, namely, the control of the regioregularity, molecular weight, and polydispersity, as well as the elimination of remnant bromide groups.
- Purification of a single molecule is in general easier than that of a polymer.

- Materials derived from molecular elemental units show in general higher charge-carrier mobilities than polymers.
- The analysis of the relationships between chemical structure, electronic properties, and device performances is more straightforward than that for polymers for which structural modifications can indirectly affect the electronic properties through changes in molecular weight, polydispersity, and effective conjugation length.
- The high molecular extinction coefficients of many molecular dyes permits limiting the thickness of the active layer, thus minimizing problems associated with charge transport and series resistance.
- Many small dye molecular structures can be viewed as quasi-spherical particles, which can be more appropriate to isotropic optical and transport properties than linearly conjugated systems.

During the past 3−4 years, the potentialities offered by molecular BHJ solar cells have been explored by several groups. In this context, the aim of this Account is to present a brief overview of this emerging area with an emphasis on the work carried out in our group.
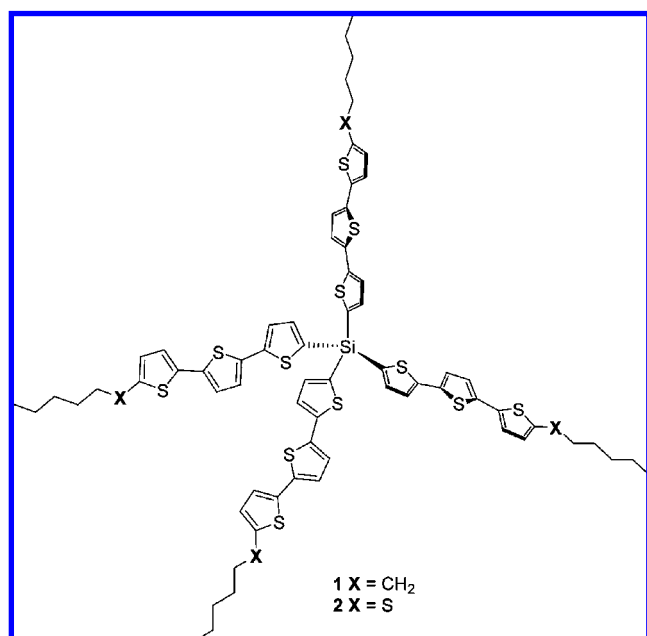
Molecular Donors in Heterojunction Solar Cells

Molecular donors have been widely used for the fabrication of bilayer heterojunction solar cells.[1−3] Such devices take advantage of the high purity and high charge-carrier mobility of molecular materials and some synthetic work has been focused on donor materials specifically designed for bilayer cells.[14,15] Planar molecules with a strong propensity to adopt a horizontal orientation on substrate can lead to efficient bilayer solar cells.[1−3,14,15] However such planar molecules are not ideal to ensure the isotropic charge transport required in BHJ. In fact, as discussed below, many donors used in efficient molecular BHJ solar cells possess a pseudo-3D geometry.[16]

Sun et al. have synthesized X-shaped conjugated systems with four linear oligothiophene chains connected to a central thiophene core. BHJ cells based on these molecules and PCBM gave a power conversion efficiency (η) of 0.80% under simulated solar illumination.[17] Lloyd et al. have reported BHJ cells based on soluble triethylsilylethinyl-anthradithiophene as donor with $\eta = 1.0\%$.[18] Dendrimers have recently been used as donors in BHJ cells with conversion efficiencies of 1.30%.[19,20] Although these systems share some of the advantages of small molecules in terms of structural definition, their synthesis is in general more complex.

Tetrahedral Conjugated Systems as Donors in BHJ Solar Cells

One of the first examples of BHJ cells based on a soluble molecular donor was reported by our group in 2005.[21] The donor consisted of four conjugated oligothiophene chains fixed onto a silicon node (**1**, **2**). The branches were end-capped with *n*-hexyl or *n*-hexylsulfanyl chains in order to increase the solubility of the system and to stabilize the cation radical by electron-releasing effects. As confirmed by cyclic voltammetry, introduction of terminal hexylsulfanyl groups in the structure leads to a fully reversible oxidation wave characteristic of a stable cation radical. Comparison of the absorption maximum of the 3D systems to those of the individual linear branches reveals a 17−19 nm red shift attributed to the inductive effect of the silane group

1 X = CH$_2$
2 X = S

FIGURE 2. Current density vs voltage curve for a bilayer heterojunction **2**/perylenediimide under white light illumination at 80 mW cm^{-2}. From ref 22, reprinted with permission from the Royal Society of Chemistry, copyright 2006.
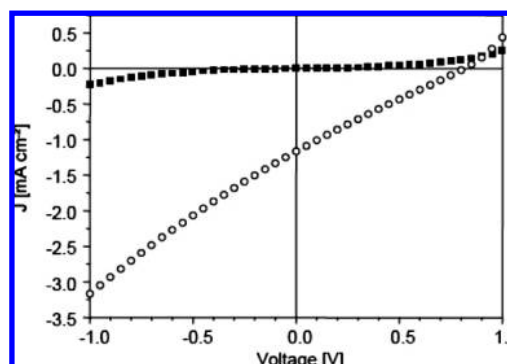
FIGURE 3. Current density vs voltage curve for a bulk heterojunction **2**/PCBM under white light illumination at 80 mW cm^{-2}. From ref 22, reprinted with permission from the Royal Society of Chemistry, copyright 2006.

Compounds **1** and **2** were first evaluated in bilayer solar cells realized by thermal evaporation of the donors and *N,N*-9-bis-tridecylperylenedicarboxyimide as acceptor. Comparison of the performances of these devices to those of reference systems based on dihexylterthienyl shows that despite comparable effective conjugation lengths, the 3D donors lead to power conversion efficiencies 4−5 times higher (Figure 2).[21]

This result has been attributed to the combined effects of a better absorption of the incident light and isotropic hole

SCHEME 1. Possible Molecular Packing of Linear (Left) and Tetrahedral (Right) Oligothiophenes in Thin Film Prepared by Thermal Evaporation under Vacuum
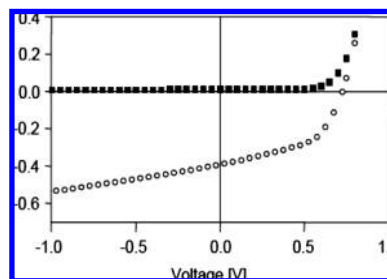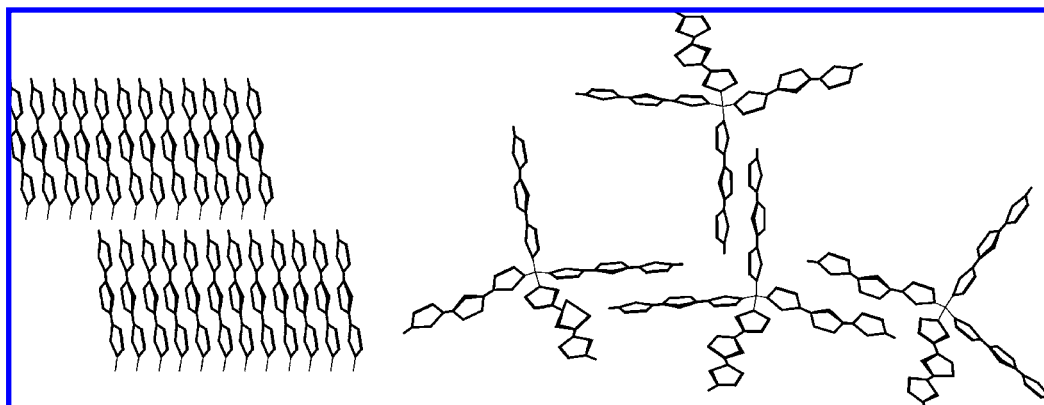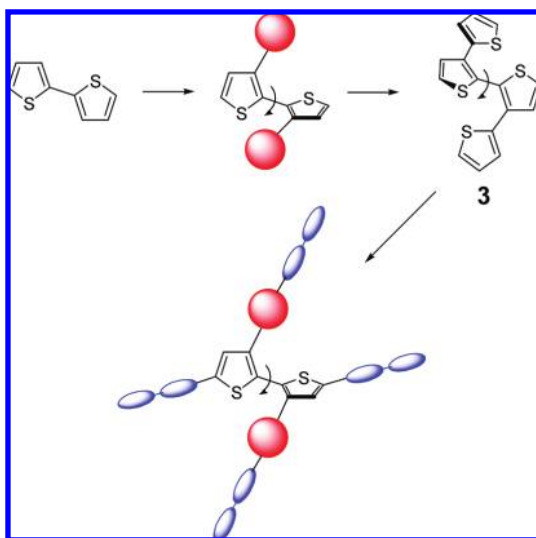
SCHEME 2. Generation of Tetrahedral Conjugated Systems Derived from a Bithiophene Node Twisted by Steric Interactions

SCHEME 3. Three-Dimensional Conjugated Systems Based on Twisted Bithiophene

transport in contrast to films of short-chain oligothiophenes in which absorption of incident light and hole transport across the cell are limited by the preferential vertical orientation of the molecules on the substrate (Scheme 1).

A prototype bulk heterojunction cell based on compound **2** and PCBM in a 1:3 w/w ratio gave a short-circuit current density of 1.13 mA cm^{-2} and a power conversion efficiency of 0.30% under simulated AM 1.5 solar irradiation (Figure 3).[22] Although modest, these first results were considered as promising taking into account the absorption maximum of the donor (390 nm). However, the insufficient robustness of the silicon–thiophene bond was identified as problematic, and in some cases degradation of the molecules was observed during vacuum sublimation.

In order to solve this problem, we have developed a different approach based on the use of a bithiophene twisted by steric effects as a node for building 3D conjugated systems (Scheme 2). The steric interactions associated with the fixation of bulky groups at the 3,3'-positions of bithiophene produce a dihedral angle between the thiophene rings, thus generating a tetrahedral starting unit for the construction of 3D systems.

While the dihedral angle was initially produced by interactions between methyl groups (**4**), in a further step, the torsion was created by interactions between thiophene rings (Scheme 3). The major advantage of this second approach based on the previously unknown quaterthiophene **3** is to produce an ideal twist angle of 90° with a thiophene unit involved in the conjugated branches as steric generator, thus limiting the introduction of inert material in the structure.[23]
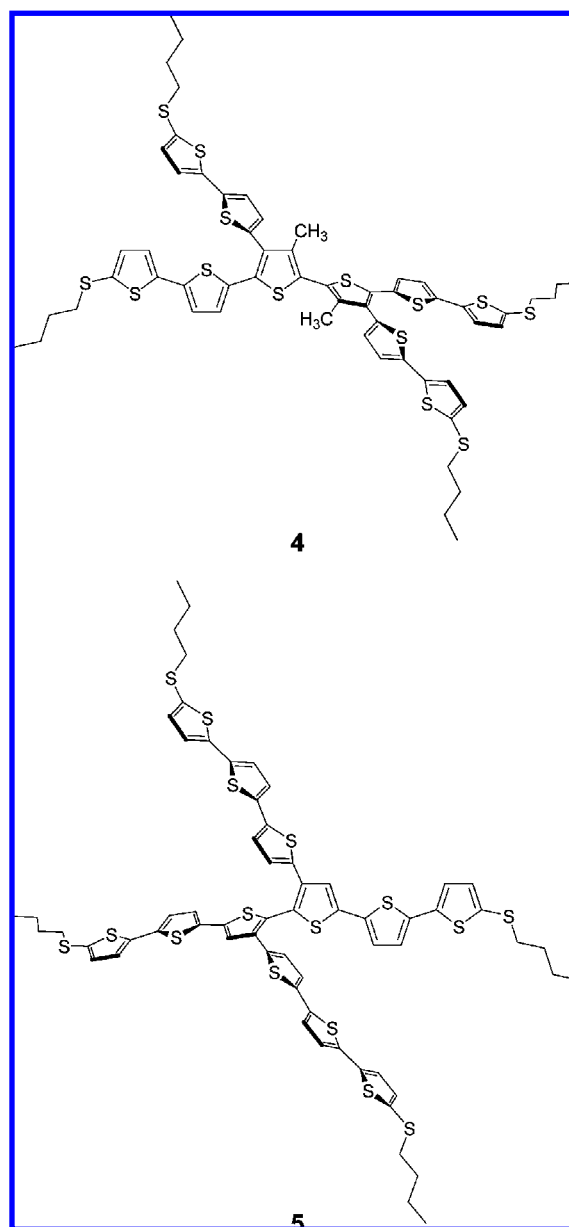
BHJ solar cells realized from chlorobenzene solutions of compound **5** and PCBM in a 1:3 w/w ratio under white light irradiation at 99 mW cm^{-2} gave a J_{sc} of 1.33 mA cm^{-2}, a V_{oc} of 0.51 V, and a power conversion efficiency of ~0.20%.[23] As for compound **2**, the modest efficiency must be considered in relation with the absorption of the donor (λ_{max} = 399 nm) (Figure 4).

Despite these limited efficiencies, the first results obtained on these model systems based on short-chain oligothiophenes confirmed the validity of the concept of 3D molecular donor. However, the low filling factor of the cells, typically ~30% represents a major weakness for these sys-
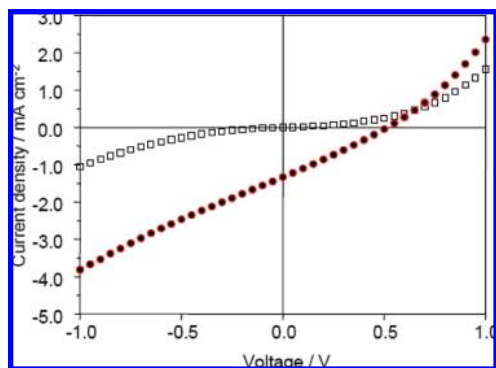
FIGURE 4. Current density vs voltage curve for a bulk heterojunction **2**/PCBM under white light illumination at 80 mW cm^{-2}. From ref 23, reprinted with permission from Wiley, copyright 2007.
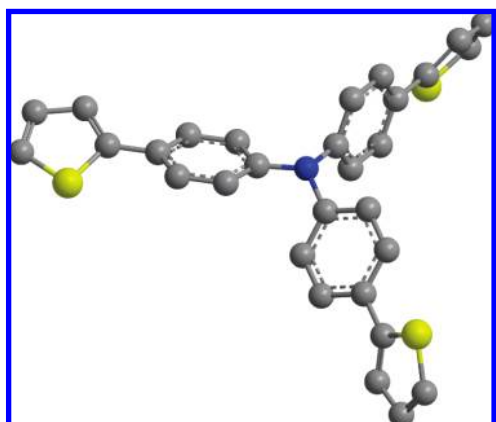

FIGURE 5. Three-dimensional model of 2-thienyl-substituted triphenylamine.

tems. This clearly indicates that besides a reduction of their energy gap, further work focused on the optimization of the hole-transporting properties of these molecular donors is needed.

Triphenylamine-Based π-Conjugated Systems as Donors for BHJ Solar Cells

Triphenylamine (TPA) derivatives have been intensively investigated as molecular and polymeric hole-transporting materials.[24] Steric interactions among phenyl groups, confere on TPA a propeller-like geometry, which represents an interesting platform for the building of pseudo-3D molecular donors (Figure 5). We have synthesized several series of hybrid conjugated systems based on various types of oligothiophene and oligothienylenevinylene conjugated branches attached on a TPA core. The charge-transport properties of these systems have been evaluated and a hole mobility of 1.1×10^{-2} cm^2 V^{-1} s^{-1} was determined on field-effect transistors based on compound **6** with terthiophene arms.[25]

While our goal was to develop donors for BHJ solar cells, several compounds could not be processed into composite films with PCBM. Consequently, compounds **6**−**10** (Scheme 4) have been evaluated in bilayer cells made by thermal evaporation of C$_{60}$ onto a film of donors. Depending on the chemical structure, films of donors were either spin-cast from chlorobenzene solutions or deposited by thermal evaporation.

As shown in Table 1, donors containing thienylenevinylene (TV) branches (**7**, **8**) lead to J_{sc} values higher than 2.0 mA cm^{-2} and to the largest conversion efficiencies. Increasing the length of the TV branches in compound **8** leads to the expected red shift of λ_{max} but does not improve J_{sc} nor efficiency.[26]

Attempts to improve the hole-transport properties of the compounds by introduction of donor groups such as 3,4-ethylenedioxythiophene (EDOT)[27] (**9**) or dithiafulvene (**10**)[28] in the structure results in a dramatic loss of conversion efficiency due in particular to a large decrease of V_{oc}. Thus, replacing the median thiophene in compound **6** by EDOT (**9**) produces a decreases of V_{oc} from 0.68 to 0.32 V, while the conversion efficiency falls from 0.36% to 0.14%. BHJ cells have been fabricated with donors **7**, **8**, and **9** using PCBM as acceptor. The results confirm the trend observed on bilayer cells and show that the highest efficiency of 0.43% is obtained with compound **7**. This result is consistent with the red-shifted absorption compared with compounds **2** and **5**. While these first results demonstrate the potential of soluble TPA-based molecular architectures as donor for BHJ solar cells, extension of the photoresponse toward longer wavelengths and improvement of the light-harvesting properties of these donors are clearly needed.

Molecular Donors with Internal Charge Transfer

A large part of the synthetic chemistry of π-conjugated donors for organic solar cells is presently focused on the synthesis of low band gap polymers in order to extend the photoresponse of solar cells toward the 600−800 nm region of the solar spectrum where the photon flux is maximum. While the synthetic principles for band gap engineering are well established,[29] the design of low band gap systems as donor for heterojunction organic solar cells imposes some specific requirements. In fact, some synthetic strategies that involve a simultaneous decrease of the LUMO level and increase of the HOMO have deleterious consequences for the voltage of solar cells, since this latter parameter depends on the difference between the LUMO of the acceptor and the HOMO of the donor.[30] Therefore, the design of low band gap conjugated systems for organic heterojunction solar cells must resort to

SCHEME 4. Star-Shaped π-Conjugated Systems Based on Triphenylamine Node
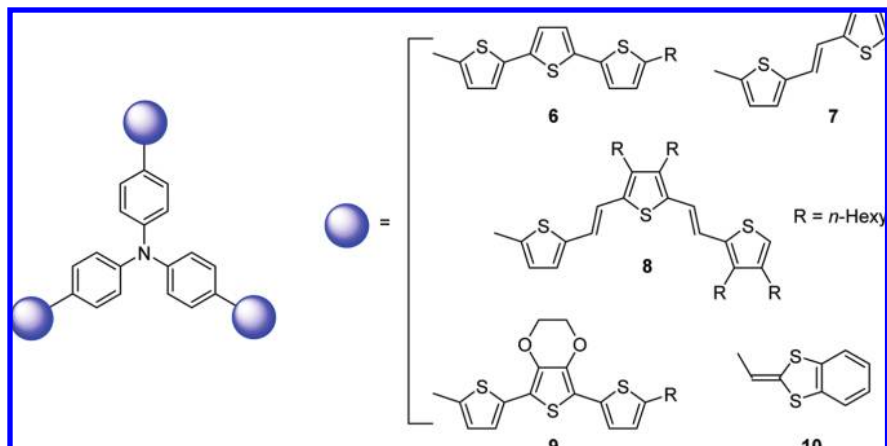
TABLE 1. Optical and Electrochemical Data for TPA Derivatives **6**−**10** and Photovoltaic Characteristics of Bilayer Solar Cells Based on These Donors with C_{60} as Acceptor[a]

compd	λ_{max} (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η (%)
6	429	1.73	0.68	29	0.36
7	424	2.33, **2.43**	0.48, **0.60**	41, **28**	0.46, **0.43**
8	477	2.22, **1.53**	0.50, **0.62**	29, **27**	0.32, **0.26**
9	438	1.50, **0.40**	0.32, **0.43**	30, **22**	0.14, **0.04**
10	398	0.87	0.40	32	0.11

[a] Data in bold type correspond to BHJ cells with PCBM as acceptor.
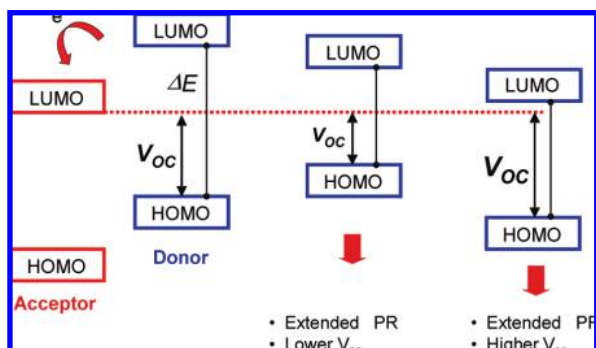
**FIGURE 6.** Engineering the band gap of π-conjugated donors for organic solar cells.

synthetic approaches in which the decrease of the HOMO−LUMO gap (ΔE) does not involve any increase of the HOMO level.[31] In fact, an ideal situation would consist in a decrease of both the HOMO and LUMO levels, with a faster decrease of the latter (Figure 6). Under these conditions, the reduction of ΔE will lead at the same time to a red shift of the photoresponse (PR) onset, to an increase of the cell voltage, and to an improvement of the chemical stability of the donor against oxygen.[31]

As an application of these principles, we have synthesized a donor derived from compound **7** in which an internal charge transfer (ICT) is created by replacing one of the terminal thiophene rings by an indanedione acceptor group (**11**).[32] The

ICT is evidenced by an additional absorption band around 540 nm in the UV−vis spectrum. As expected, the introduction of the acceptor group increases the oxidation potential from 0.62 to 0.72 V vs Ag/AgCl. The external quantum efficiency (EQE) spectrum of a BHJ solar cell based on donor **7** exhibits a broad maximum of ∼20% in the 350−450 nm range. The presence of indanedione in the structure leads at the same time to an enhancement of EQE in the 350−450 nm region and to the emergence of a intense new active band corresponding to the ICT in the 500−700 nm region (Figure 7).

Under simulated solar irradiation, the *J* vs *V* characteristics of BHJ cells based on donors **7** and **11** show that the broadening and red shift of the EQE spectrum results in a large improvement of the cell performance (Figure 8). Thus, the power conversion efficiency increases from 0.41% to 0.81% due to a concomitant increase of J_{sc} from 2.43 to 4.10 mA cm^{-2} and of V_{oc} from 0.60 to 0.66 V.[32]
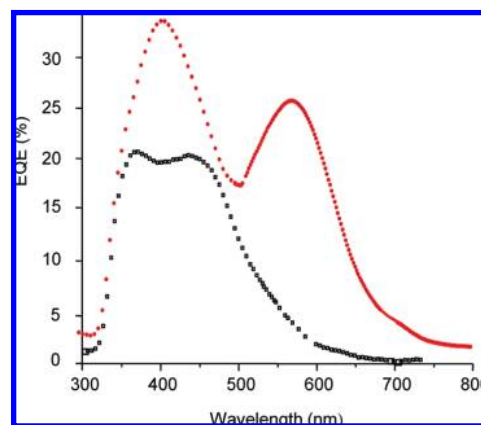
FIGURE 7. External quantum efficiency of BHJ solar cells donor/ PCBM (1:3): (□) donor **7**; (red ●) donor **11**. Reprinted with permission from ref 32. Copyright 2006 American Chemical Society.
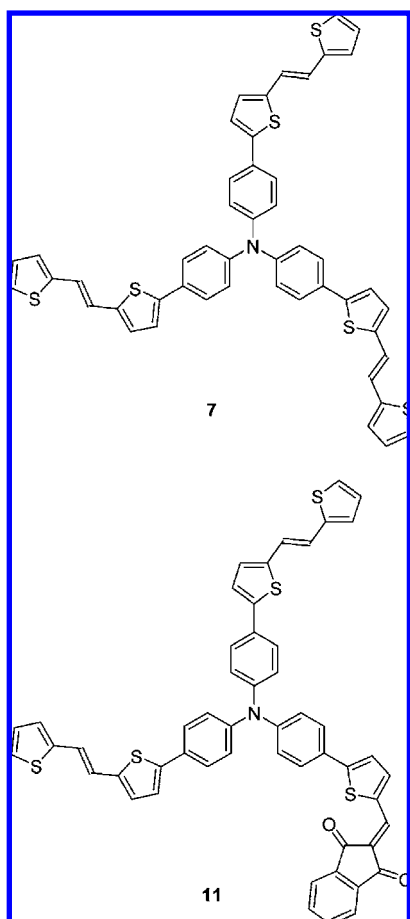
The molecular engineering of ICT in TPA-based systems was analyzed in more detail by introducing an increasing number of acceptor groups in the donor structure. For practical synthetic reasons, the dicyanovinyl group was used for this purpose, with however an undesired effect of a decrease of the compatibility of the donor with PCBM. Consequently, these new donors could not be evaluated in BHJ but in bilayer cells.
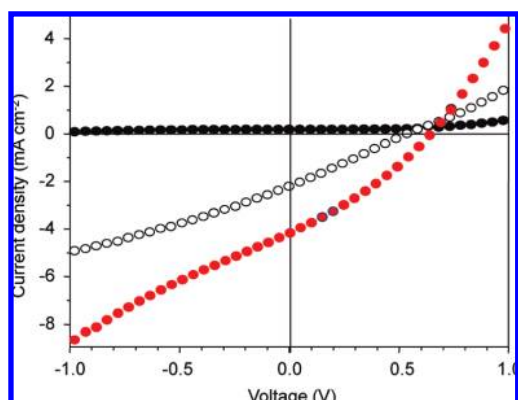

FIGURE 8. Current density vs voltage characteristics of BHJ solar cells donor/PCBM (1:3) in the dark (●) and under white light illumination at 100 mW cm^{-2}: (○) donor **7**; (red ●) donor **11**. Reprinted with permission from ref 32. Copyright 2006 American Chemical Society.

As shown by UV−vis spectra, the progressive replacement of the thienylenevinylene groups by dicyanovinyl induces a concomitant decrease of the intensity of the $\pi-\pi^*$ transition and intensification of the ICT band, which becomes predominant after introduction of three acceptor groups (Figure 9).

Cyclic voltammetry shows that the introduction of dicyanovinyl groups in the structure leads to an increase of the redox potential from 0.62 V for compound **7** to 1.06 V for compound **14**. However, this increase is not accompanied by a destabilization of the cation radical since the CV of compound **14** remains fully reversible.[32]

This series of donors has been evaluated in bilayer cells fabricated by thermal evaporation of a C_{60} layer on top of a film of donor. The EQE spectra show that the intensification of the ICT band results in a progressive shift of the maximum EQE peak toward longer wavelengths.[32] The results obtained under white light illumination confirm the progressive increase of the power conversion efficiency due to the combined effects of the red shift of the EQE spectrum and increase of the cell voltage. Thus, an efficiency of 1.85% and a V_{oc} as high as 1.15 V have been obtained with donor **14**. Interestingly, this latter device also works as a red light-emitting diode with high spectral purity under positive polarization.[33]

This approach has been extended to the synthesis of new series of donors with ICT containing stronger electron acceptors such as tricyanovinyl groups. However, these compounds could not be used as donor in BHJ solar cells because they are stronger acceptors than C_{60}.[34] Work devoted to their possible use as acceptor materials is in progress and will be reported in future publications.

In summary, these first results have shown that TPA represents an interesting core for the design of molecular donors and that the creation of an ICT in the donor structure produces simultaneously a bathochromic shift of the absorption onset, an improvement of the light-harvesting properties and an increase of the cell voltage that result in a considerable improvement of conversion efficiency. An efficiency of 0.80% has been obtained for a BHJ cell, while a value of 1.85% was obtained for a bilayer cell based on a donor with optimized ICT. Taking into account the fact that BHJ cells are in general much more efficient than bilayers based on the same active materials, this latter result suggests that provided problems of processability can be resolved, this class of molecular donors has a large potential of progress, as confirmed by the increasing number of publications on this class of materials published in the past two years.
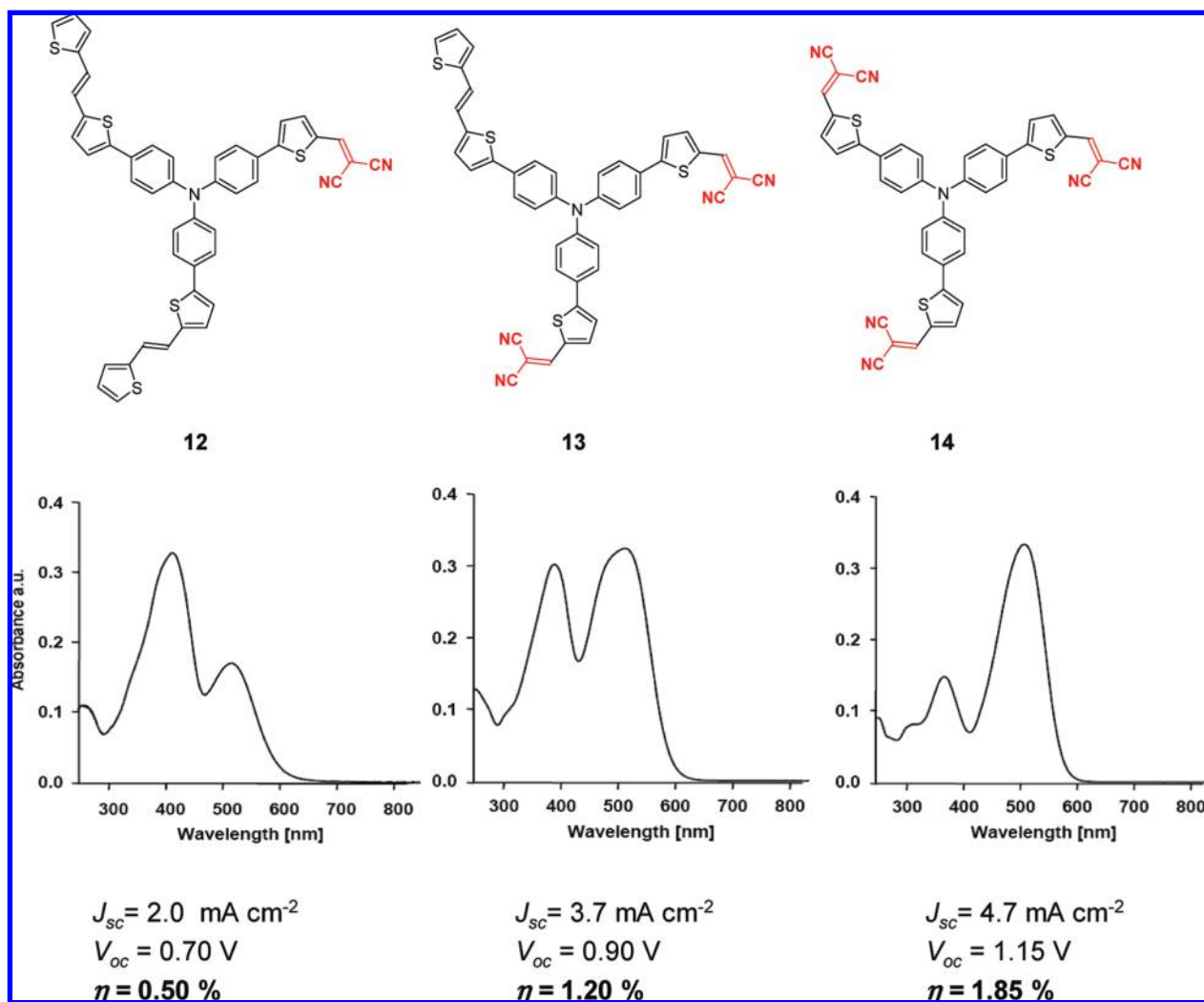
FIGURE 9. Effect of the introduction of dicyanovinyl groups in the structure on the UV−vis absorption spectrum of the donor and on the characteristics of bilayer solar cells donor/C_{60} under white light irradiation at 100 mW cm^{-2}Reprinted with permission from ref 32. Copyright 2006 American Chemical Society.
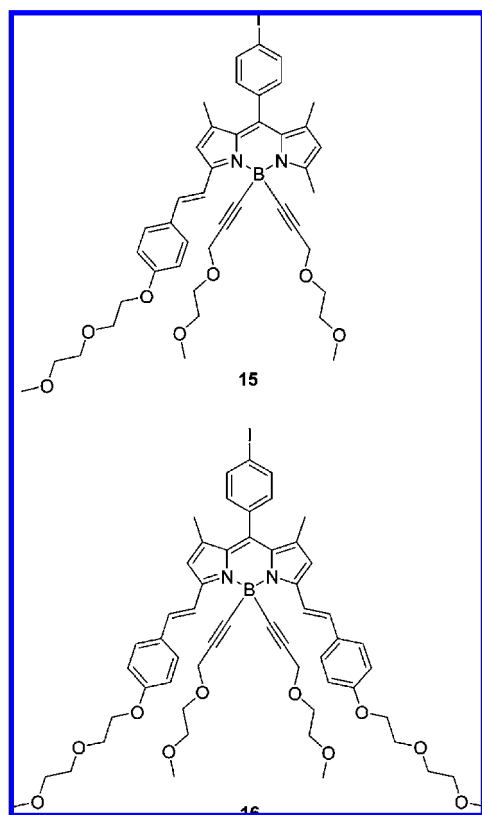
BODIPY Derivatives as Donors in BHJ Solar Cells

Derivatives of borondipyrromethene (BODIPY) form an important class of dyes subject to considerable interest owing to a unique combination of facile synthesis, stability, high absorption coefficient, and high photoluminescence efficiency.[35] On the other hand, based on the presence of a tetrahedral boron atom in the structure, BODIPY appears as an interesting starting platform for the development of isotropic active materials for (opto)electronic devices and solar cells.

In a first exploration of the potentialities of this class of molecular donors, BHJ solar cells have been realized using extensively conjugated BODIPY derivatives **15** and **16** as donor and PCBM as acceptor. The introduction of one or two styryl units in the structure permits modulation of the HOMO−LUMO gap, while the solubility and film-forming properties of the molecules are brought by the oligooxyethylene chains. The UV−vis spectra show maxima at 572 and 646 nm with high molecular extinction coefficients (ε_{max} = 96 500 and 135 000 M^{-1} cm^{-1}) and high photoluminescence quantum yields (0.75 and 0.46) for compounds **15** and **16** respectively. Both compounds are reversibly oxidized around 0.60−0.75 V and reversibly reduced in the −1.20 to −1.30 V region. The UV−vis spectra of thin films spin-cast on ITO glass lead to band gap values of E_g = 1.95 and 1.70 eV for **15** and **16**, respectively.

BHJ cells were fabricated with these two donors and PCBM in a 1:0.8 w/w ratio. The EQE spectrum of the cell based on compound **15** shows a first maximum of 27% around 450 nm followed by a more intense peak of 45% around 570 nm. For compound **16**, the spectrum shows an intense first peak of ∼40% at 400 nm and a second peak of 32% around 680

FIGURE 10. External quantum efficiency (top) of BHJ cells based on donor **14** (−−−) and **15** (—), ratio donor/PCBM (1:3), and current density vs voltage curve (bottom) for a BHJ cells based on donor **15** under white light illumination at 100 mW cm^{-2}. From ref 36, reprinted with permission from the Royal Society of Chemistry, copyright 2009.

nm corresponding to the main absorption band (Figure 10). The current density vs voltage characteristics under white light illumination at 100 mW cm^{-2} show that both devices give short-circuit current densities exceeding 4.0 mA cm^{-2}. The cell based on donor **15** delivers an open-circuit voltage of 0.796 V and a filling factor of 34% leading to a power conversion efficiency of 1.17%. For donor **16**, the cell shows a lower V_{oc} of 0.753 V, in agreement with the higher HOMO level, but a better FF value of 44%, giving a conversion efficiency of 1.34%.[36]

These good performances obtained with molecules with relatively narrow absorption bands suggest that this class of compounds possess a huge potential and that BODIPY represents an attractive platform for the design of soluble 3D molecular donors. A particularly interesting feature concerns the multiple possibilities of derivatization that could allow a fine tuning of the relevant parameters of solar cells such as light absorption, open-circuit voltage, and hole transport almost independently. This possibility to disconnect parameters that are tightly interdependent in polymers can allow the fabrication of BHJ solar cells using mixtures of dyes with complementary absorption properties but small differences in energy levels.

In order to test this idea, we have fabricated multidonor BHJ cells using a combination of compounds **15** and **16** as
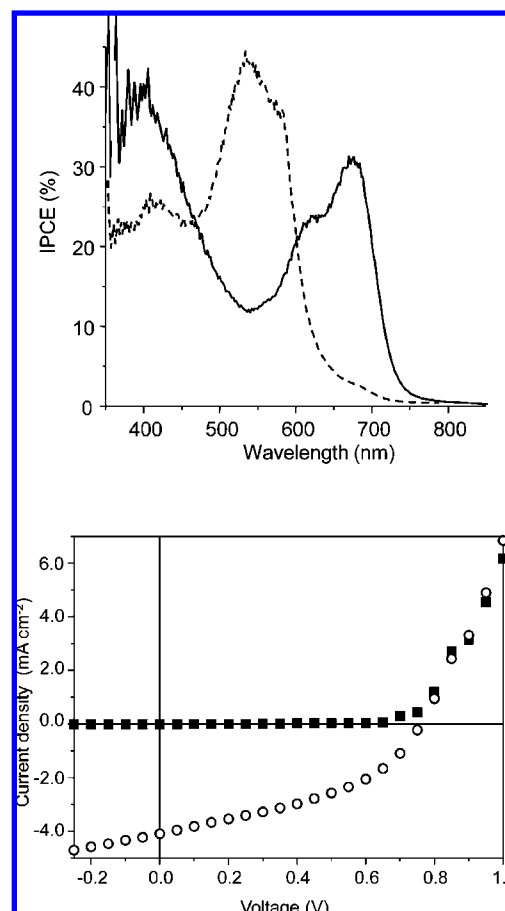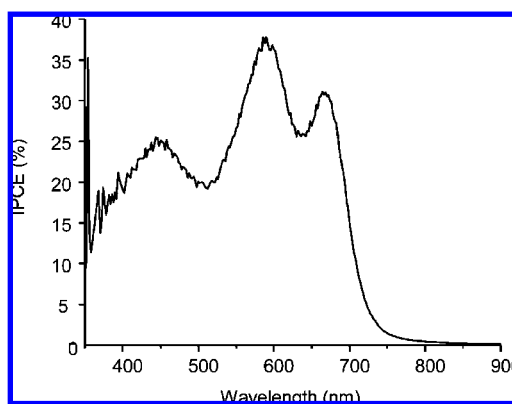

FIGURE 11. External quantum efficiency of a BHJ cell based on donors **14** and **15** and PCBM (1:1:2 in weight). From ref 37, reprinted with permission from the Royal Society of Chemistry, copyright 2009.

donor material. The EQE spectrum clearly evidenced the contribution of the two dyes (Figure 11), while a power conversion efficiency of 1.70% was obtained under white light

illumination.[37] This value, which equaled the record efficiency reported a few weeks earlier for cells based on merocyanine dyes,[38] has been recently surpassed by the 3.0% efficiency reported for a cell based on an oligothiophene containing a diketo-pyrrolo-pyrrole as donor.[39]

Conclusions and Outlook

Interdisciplinary research effort focused on the analysis of the various elemental mechanisms involved in the photon−electron conversion process and on the technology of organic solar cells has generated considerable progress allowing power conversion efficiencies to increase from 0.10% to more than 5% in ca 10 years. This progress has been accomplished with a few donor materials that progressively became standards because they combine good optical, charge-transport, and mechanical properties with commercial availability in large quantities. However, the development of organic solar cells has now reached a turning point where efficiency is approaching the limit imposed by the physical properties of these standard materials and where further progress now requires the creation of new generations of active materials. While the synthesis of low band gap polymers represents one of the main routes for future research, the problems posed by the control of the regioregularity, molecular weight, polydispersity, and purification of polymers will remain important issues. In this context, the development of BHJ solar cells based on soluble molecular donors represents a plausible alternative to bypass the problems inherent to polymers. Indeed, new molecular materials that would ideally combine unequivocal chemical structure, straightforward and cost-effective synthesis, ease of purification, processability, high absorption coefficients, and isotropic optical and charge-transport properties can significantly contribute to solve some of the key problems posed by the fabrication of BHJ solar cells.

The validity of these ideas was demonstrated in seminal work published a few years ago on molecular BHJ cells with conversion efficiencies of ~1%, while the introduction of internal charge transfer in the donor structure has contributed to enlarge the possibilities of the molecular engineering of these donor materials. These new research areas have become a focus of high current interest as attested by the increasing number of papers published on these topics during the recent period. On the other hand, these new aspects of the design of molecular donors have changed our view of some well-known families of dye molecules that have recently been used as donors in highly efficient BHJ solar cells.

Only four years after the initial reports, molecular BHJ cells have already reached the efficiency of polymeric BHJ cells a few years ago, when replacement of PPV derivatives by P3HT allowed push conversion efficiency to be pushed from 2−3% to 5%. Research on molecular BHJ cells has just begun; based on the multiple potential advantages of this approach, there little doubt that research in this area will intensify in the coming years. While some promising basic structures have already been identified and are now under optimization, creative molecular design and synthetic chemistry are required more than ever.

BIOGRAPHICAL INFORMATION

Jean Roncali received his Ph.D. from the University of Paris 13 under the supervision of Francis Garnier. After successive positions as technician, engineer, and Associate Researcher in the Laboratory of Molecular Materials of CNRS, he moved to the University of Angers in 1991 where he became Director of Research and created the Linear Conjugated Systems Group. His research interests encompass the development of functional π-conjugated systems with tailored electronic properties in view of applications in solar energy conversion, electronic and photonic devices, and nanosciences.

FOOTNOTES

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