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Triphenylamine−Thienylenevinylene Hybrid Systems with Internal Charge Transfer as Donor Materials for Heterojunction Solar Cells

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Abstract: Star-shaped molecules based on a triphenylamine core derivatized with various combinations of thienylenevinylene conjugated branches and electron-withdrawing indanedione or dicyanovinyl groups have been synthesized. UV−vis absorption and fluorescence emission data show that the introduction of the electron-acceptor groups induces an intramolecular charge transfer that results in a shift of the absorption onset toward longer wavelengths and a quenching of photoluminescence. Cyclic voltammetry shows that all compounds present a reversible first oxidation process whose potential increases with the number of electron-withdrawing groups in the structure. Prototype bulk and bilayer heterojunction solar cells have been realized using fullerene C_{60} derivatives as acceptor material. The results obtained with both kinds of devices show that the introduction of electron-acceptor groups in the donor structure induces an extension of the photoresponse in the visible spectral region, an increase of the maximum external quantum efficiency, and an increase of the open-circuit voltage under white light illumination. These synergistic effects allow reaching power conversion efficiencies of ∼1.20% under simulated AM 1.5 solar irradiation at 100 mW cm^{-2}.

Introduction

Organic semiconductors based on π-conjugated systems are intensively investigated as active materials in organic field-effect transistors (OFETs) and light-emitting diodes.[1,2] Combined with substrates such as polymer films or paper, these materials allow envisioning the development of lightweight flexible devices such as intelligent paper, displays, tags, or RFID by rather simple and low-energy-demanding technologies. In this context, organic solar cells investigated for fundamental reasons or with the long-term goal of developing low-cost renewable energy sources could also find a niche as power supplies in the emerging area of flexible (opto)electronics.

While a donor−acceptor heterojunction with a power conversion efficiency of 0.95% was reported in 1986 by Tang,[3] it is only recently that the performances of this type of solar cell have been significantly improved to reach efficiencies in the 3−4% range.[4] The discovery of ultrafast and ultraefficient photoinduced electron transfer between π-conjugated polymers and fullerene derivatives[5] has generated considerable interest for bulk heterojunction solar cells based on interpenetrating networks of conjugated systems and C_{60} derivatives.[6,7] During the past decade, intensive research effort invested in the understanding and technological optimization of these devices[7−9] has generated a continuous improvement of performances which now reach power conversion efficiencies of 4−5%.[9] Whereas a small number of donor and acceptor materials such as phthalocyanines,[4,10] poly(*p*-phenylenevinylenes), poly(thiophenes),[6−9] perylene,[4,10] or fullerene derivatives[6−9] have led to the fabrication of efficient devices, over the longer term the development of a chemistry focused on the design of materials specifically tailored for photovoltaic conversion can be expected to significantly contribute to the progress of the field. Recent work in this area has been focused on the synthesis of new donor or acceptor compounds,[11] molecular or supramolecular archi-

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10.1021/ja058178e CCC: $33.50

tectures combining donor and acceptor blocks,[12] or conjugated polymers with reduced band gaps.[13]

Organic semiconductors based on low-dimensional π-conjugated systems such as oligothiophenes are known to present highly anisotropic electronic properties.[1] This point has been clearly demonstrated on OFETs based on sublimed thin films of oligothiophenes for which the highest hole mobility is observed when the molecules are oriented perpendicularly to the substrate.[1,14] However, such an orientation is detrimental for solar cells because it strongly reduces the absorption cross section for the incident light as well as the efficiency of charge transport through the cell thickness.[15,16] A first solution to this problem consists of using as active materials two-dimensional conjugated systems prone to adopt an horizontal orientation on the surface, for example phthalocyanines,[3,4,10] or more recently hexabenzocoronenes,[11a] or planarized star-shaped oligothiophenes.[11b,16]

Another possible solution would consist in the development of organic semiconductors in which the anisotropy of electronic properties (and hence the need to control molecular orientation) would be reduced by an increase of the dimensionality of the elemental unit. As a first step in this direction, we have recently shown that three-dimensional (3D) conjugated architectures in which four oligothiophene chains are attached to a silicon node lead to promising results as donors in bulk heterojunction solar cells.[17]

Organic glasses derived from triphenylamine (TPA) derivatives have been widely investigated for almost two decades.[18] Considerable effort in synthetic chemistry, in particular by Shirota and co-workers, has led to the development of many classes of TPA-based compounds as hole-transporting or electroluminescent materials.[18] Owing to the noncoplanarity of the three phenyl substituents, TPA derivatives can be view as 3D systems. The combination of TPA with linear π-conjugated systems could be expected to lead to amorphous materials with isotropic optical and charge-transport properties. Star-shaped molecules consisting of a TPA core substituted by oligophenylenes, 2-phenylthiophene, or fluorene have been described,[18−20] and the first examples of OFETs based on materials containing the TPA core have been recently reported.[20] However, the use of TPA-based materials for photovoltaic conversion has been scarcely considered. TPA-based starburst molecules containing nitro or dimesitylboryl acceptor groups have been synthesized.[18] When used as donors in bilayer heterojunctions, these compounds led to conversion efficiencies of 0.4 and 0.1% under monochromatic irradiation at 440 nm where the molecules mainly absorb.[18]

We now report the synthesis of hybrid donor compounds consisting of various combinations of a TPA core derivatized with dithienylethylene π-conjugated chains and electron-acceptor groups (Chart 1). These systems have been designed in order to (i) take advantage of the hole-transport properties of TPA derivatives[18−20] and oligothienylenevinylenes,[21] (ii) extend the absorption spectrum of the donor toward longer wavelengths by an intramolecular charge transfer,[13] and (iii) confer a high oxidation potential on the donor and thus preserve a high open-circuit voltage for the resulting solar cells.[22]

The electronic properties of the new compounds have been analyzed by UV−vis absorption spectroscopy, fluorescence emission spectroscopy, and cyclic voltammetry. The potentialities of these materials for photovoltaic conversion have been evaluated on prototype bulk and bilayer heterojunction solar cells using fullerene C_{60} derivatives as the acceptor, and the results are discussed in relation to the chemical structure of the donor.

Results and Discussion

Synthesis. The synthesis of the target molecules is depicted in Scheme 1. All final compounds derive from the key trialdehyde **8** obtained in two steps from commercially available tribromotriphenylamine **12**. A Stille coupling between tributyltinthiophene **11** and compound **12** gave tris[4-(2-thienyl)-phenyl]amine[19b,23] **9** in 85% yield. Vilsmeier−Hack formylation of compound **9** led to tris[4-(5-formyl-2-thienyl)phenyl]amine **8** in 90% yield.

The use of different experimental conditions for the Wittig−Horner olefination of trialdehyde **8** with phosphonate **10**[24] led to compounds **7**, **6**, and **1** corresponding to the mono-, bis-, and tris-olefination of trialdehyde **8**. Thus, the use of 5 equiv of phosphonate **10** gave after 1 h reaction compound **1** in 70% yield. The use of 2.5 equiv of **10** and 12 h reaction led to compounds **1** and **7** in 50 and 20% yield, respectively. Finally, 2 equiv of phosphonate **10** and 15 h reaction led to a mixture

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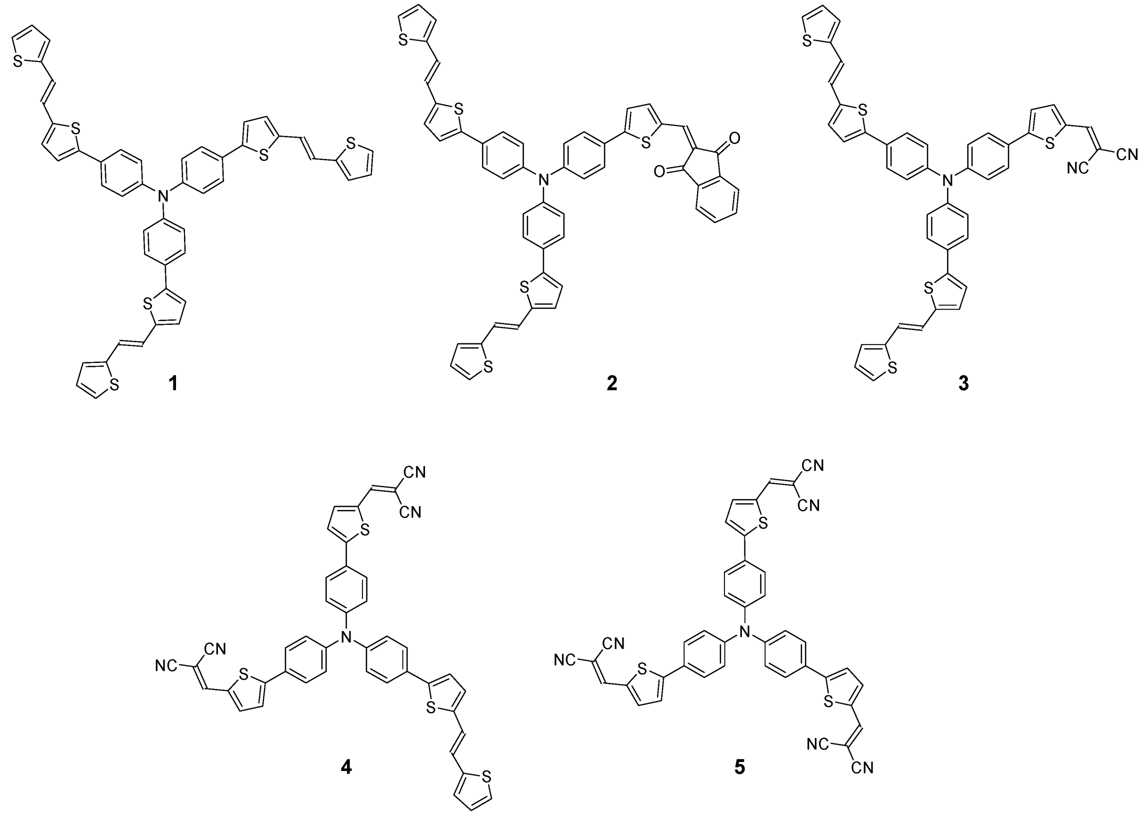
Chart 1



containing 37% compound **6**, 19% compound **7**, and 13% compound **1**. These various compounds were easily separated by column chromatography thanks to the remaining aldehyde groups on compounds **6** and **7**. Finally, compounds **2** (43%), **3** (19%), **4** (48%), and **5** (76%) were obtained by Knoevenagel condensation of indanedione or malononitrile with the appropriate aldehyde.

Optical Properties. Table 1 lists the UV−vis absorption and fluorescence emission data for compounds **1**−**5**. The spectrum of the reference compound **1** shows a single absorption band corresponding to a $\pi-\pi^*$ transition with λ_{max} at 424 nm. As shown in Figure 1, introduction of electron-withdrawing groups in the structure produces the emergence of a new transition around 500 nm assigned to an intramolecular charge transfer (ICT) between the TPA−thienylenevinylene donor part of the molecule and the acceptor end groups. The spectrum of compound **2** is quite similar to that of compound **3** (see Supporting Information). Comparison of the spectra of compounds **3**, **4**, and **5** shows that the progressive replacement of the thienylenevinylene groups by the dicyanovinyl ones induces a concomitant decrease of the intensity of the $\pi-\pi^*$ transition and an increase of the intensity of the ICT band. As shown by the data in Table 1, these changes are accompanied by an hypsochromic shift of both the $\pi-\pi^*$ and ICT bands while the energy difference between the maximum of the two transitions (ΔE) increases.

The fluorescence emission properties of compounds **1**−**5** have been analyzed in methylene chloride using anthracene as a standard. Compound **1** presents a fluorescence efficiency ϕ_{em} close to 0.40 (Table 2). This value, much higher than that of the two individual constitutive parts (dithienylethylene $\phi_{em} \sim 0.06$)[25] and TPA ($\phi_{em} = 0.06$),[26] shows that the combination of the two building blocks considerably enhances the photoluminescence efficiency as already observed for combinations of TPA and oligothiophenes.[26] All compounds containing electron-acceptor groups present an emission maximum red shifted by ca. 100 nm and a strong quenching of luminescence in agreement with the occurrence of an ICT process, as reported for bipolar compounds combining TPA and the benzothiadiazole acceptor group.[27]

For compounds **3** and **4** the emission maximum was observed only in apolar toluene, whereas in dichloromethane only a weak emission originating from the $\pi-\pi^*$ transition was observed (see Supporting Information). It is noteworthy that the quenching of luminescence is of much less magnitude in the case of compound **5** with three dicyanovinyl groups ($\phi_{em} = 0.15$). Although we have no definitive explanation for this result, the C_3 symmetry of the molecule probably plays a major role.

The band gap (E_g) of compounds **1**, **3**, **4**, and **5** has been determined from the optical spectrum of thin films prepared on glass by thermal evaporation under high vacuum (taking the intercept of the tangent to the low-energy side of the optical spectrum with the *x*-axis; see Supporting Information). As shown in Table 1, increasing the number of acceptor groups in the structure produces at the same time a blue shift of the λ_{max} of the ICT band and a decrease of E_g. This unexpected result indicates that the strength of intermolecular interactions in the

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Scheme 1

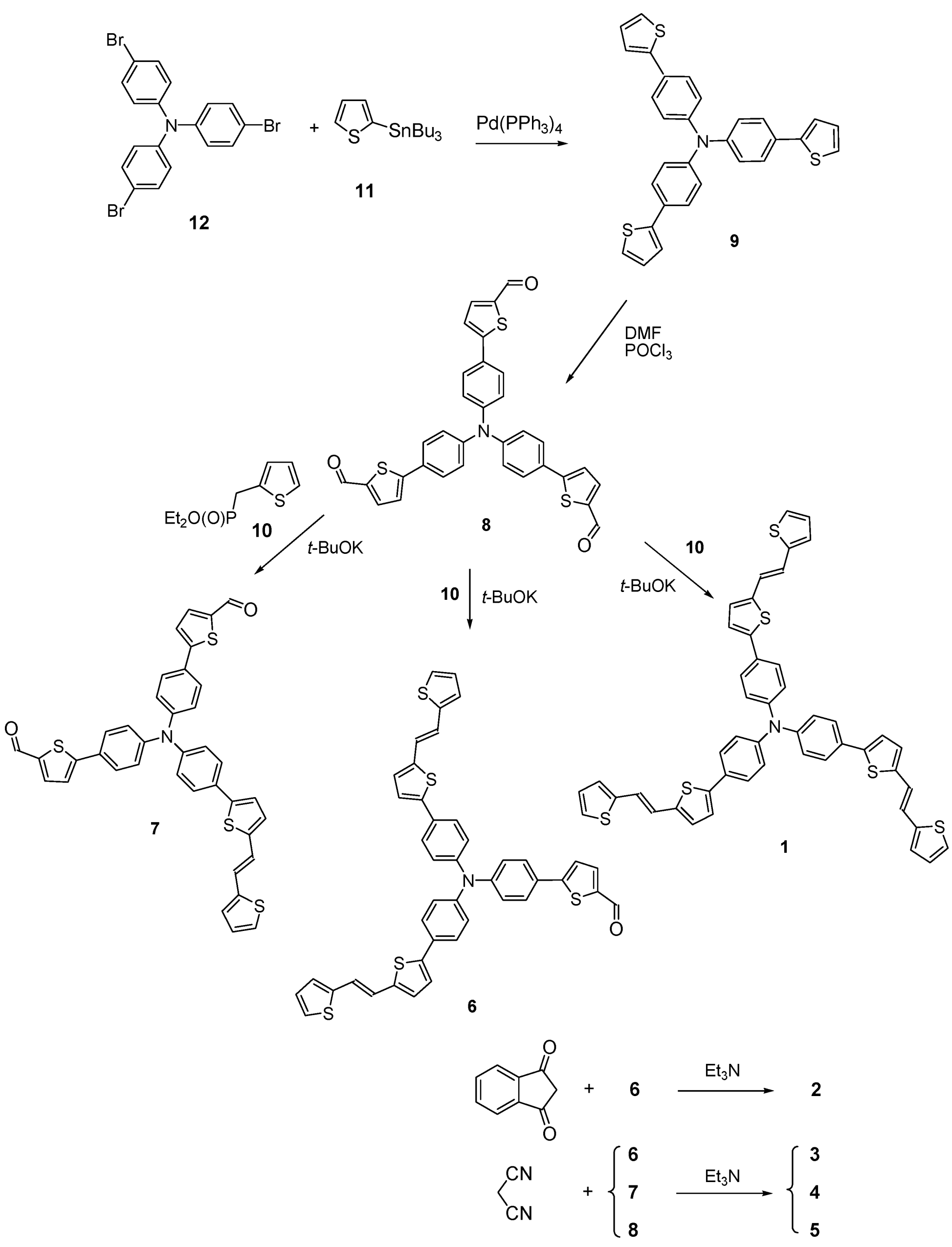

Table 1. UV−Vis Absorption and Fluorescence Emission[a] Data for Compounds **1**−**5** in CH_2Cl_2

compd	$\lambda_{max}(\pi-\pi^*)$ (nm)	λ_{max}(ICT) (nm)	ΔE^c (eV)	E_g (eV)	λ_{em} (nm)	ϕ_{em}
1	424 (435)[b]			2.38	506	0.39
2	419	536	0.65		610[c]	0.01
3	415 (426)	516 (544)	0.59	1.91	620[c]	0.01
4	390 (404)	513 (540)	0.76	1.84	632	0.01
5	368 (382)	509 (538)	0.93	1.78	636	0.15

[a] Using anthracene as a standard. [b] Values in parentheses have been measured on films. [c] ΔE corresponds to the energy difference between the maxima of the $\pi-\pi^*$ and ICT bands in solution.

solid state increases with the number of acceptor groups in the molecule. This phenomenon could reflect the development of intermolecular donor−acceptor interactions between the electron-rich inner part of one molecule and the electron-deficient peripheral part of neighbor molecules. Further work is needed to test this hypothesis.

Cyclic Voltammetry. The electrochemical properties of compounds **1**−**5** have been analyzed by cyclic voltammetry (CV) in methylene chloride in the presence of Bu_4NPF_6 as supporting electrolyte. The CV of the reference compound **1** shows a reversible oxidation process associated with the generation of the cation radical at a redox potential $E°$ of 0.62 V (Figure 2). As shown by the data in Table 2, replacement of a thienylenevinylene group by an electron-withdrawing group in compounds **2** and **3** produces a positive shift of $E°$ of 100 and 90 mV, respectively. Further increase of the number of

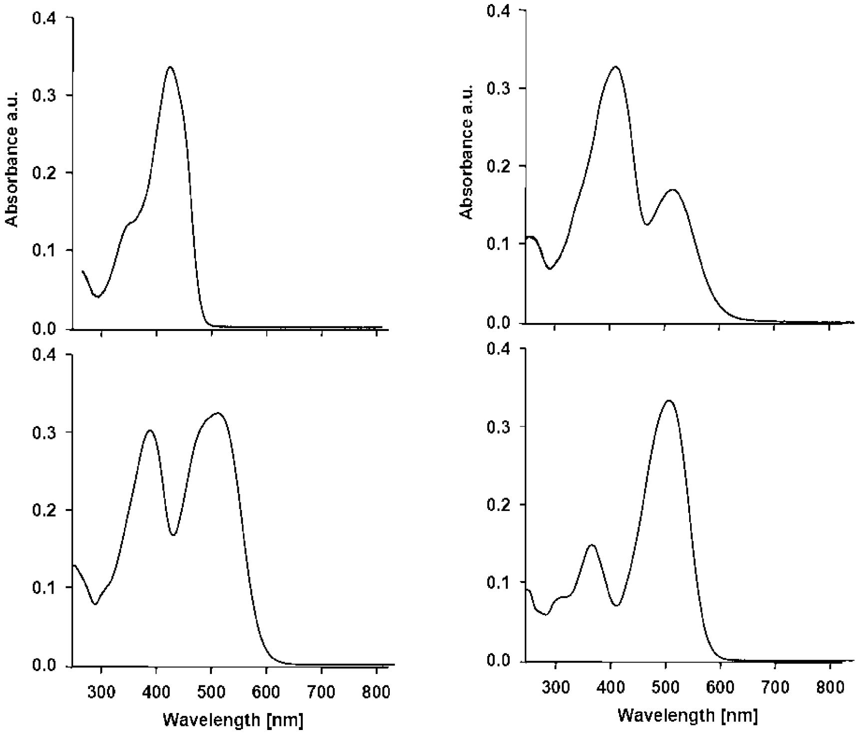

Figure 1. UV−vis absorption spectra recorded in CH_2Cl_2. Top: left, **1**; right, **3**. Bottom: left, **4**; right, **5**.

Table 2. Cyclic Voltammetric Data for Compounds **1**−**5** in 0.10 M Bu_4NPF_6/CH_2Cl_2, Scan Rate 100 mV s^{-1}, and Reference Electrode Ag|AgCl

compd	$E°$ (V)	E_{pc} (V)
1	0.62	n.d.
2	0.72	n.d.
3	0.71	−1.37
4	0.87	−1.25
5	1.06	−1.23

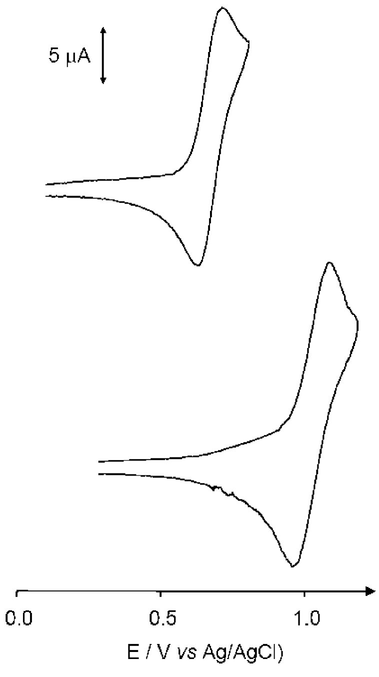

Figure 2. Cyclic voltammograms recorded in 0.10 M Bu_4NPF_6/CH_2Cl_2; scan rate 100 mV s^{-1}. Top, **1**; bottom, **5**.

acceptor groups in the structure leads to a larger shift of $E°$ with an overall increase of 0.44 V between compounds **1** and **5** (Figure 2 and Table 2).

The CV of compounds **3**−**5** exhibits an irreversible cathodic wave at a peak potential (E_{pc}) which shifts positively from −1.37 to −1.23 V when the number of dicyanovinyl groups is increased from 1 to 3. These E_{pc} values are close to those reported by Sun et al. for compounds combining TPA and dicyano acceptor groups.[28]

Photovoltaic Properties. The potentialities of donors **1**−**5** for photovoltaic conversion have been evaluated on two series of prototype heterojunction solar cells. Compounds **1** and **2** have been used for the realization of bulk heterojunctions by spin-casting composite films of the donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM)[29] as acceptor in a 1:3 ratio. On the other hand, due to the lower solubility of compounds containing dicyanovinyl groups and to problems related to the compatibility with PCBM (formation of aggregates in solution), the photovoltaic properties of compounds **3**, **4**, and **5** have been analyzed on bilayer heterojunctions realized by successive thermal evaporation of layers of the donor and fullerene C_{60} under high vacuum. The eventual crystallinity of compounds **1**−**5** has been investigated by powder X-ray diffraction studies on thin film evaporated on glass under high vacuum. For all compounds, the absence of reflection peaks in the spectra confirmed the expected amorphous character of the materials.

The photocurrent action spectra under monochromatic irradiation of the cells based on donors **1** and **2** are shown in Figure 3. For donor **1**, the spectrum exhibits a broad plateau in the 350−450 nm range with two maxima corresponding to an external quantum efficiency (EQE) of ca. 20%. Comparison with the optical spectrum of Figure 1 shows that two EQE maxima coincide with the two absorption maxima of the donor. However,

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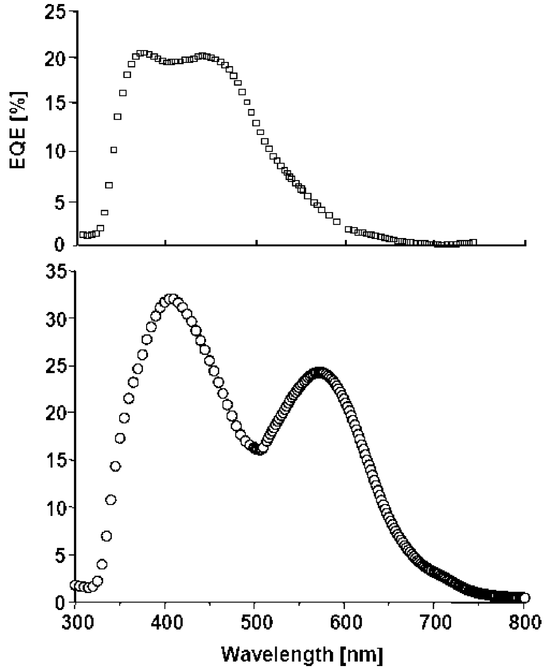

Figure 3. Photocurrent action spectra of bulk heterojunctions of donors **1** (top) and **2** (bottom) and PBCM (ratio 1:3) under monochromatic irradiation.

the first band probably contains also a significant contribution from PCBM. The action spectrum of the cell based on donor **2** exhibits two distinct bands with maxima at 410 and 550 nm. Again, examination of Figure 1 shows that these two bands correspond to the $\pi-\pi^*$ and ICT bands in the UV−vis spectrum. Comparison of the action spectra of the two cells shows that the introduction of the acceptor group in the donor structure produces an enhancement of EQE around 400 nm with a maximum of ∼33%. Interestingly, irradiation in the ICT band generates also a large photocurrent with an EQE of ca. 25% around 600 nm. This result shows that the ICT in compound **2** extends the photoresponse of the cell in the long wavelength region with ca. 100 nm red shift of the photocurrent onset up to ∼780 nm.

Figure 4 shows the current-density (J_{sc}) vs voltage (V) curves of the two cells under AM 1.5 simulated solar illumination at an intensity of 100 mW cm^{-2}. For compound **1**, the curve recorded in the dark shows an onset of rectification beyond +0.70 V, while for compound **2** the curve is fully symmetrical. For both donors the curve recorded under white light irradiation exhibits a persistent slope at negative voltage. This effect can result from various factors such as low shunt resistance, high series resistance, electron−hole recombination, or photoconductivity. Further work is required to clarify this point.

The cell based on donor **1** delivers a short-circuit current density (J_{sc}) of 2.43 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 0.60 V. Combined with a filling factor (FF) of 0.28, these data lead to a power conversion efficiency (η) of 0.41%. The J/V curve of the cell based on donor **2** reveals an increase of J_{sc} to 4.10 mA cm^{-2} and an increase of V_{oc} to 0.66 V. These data together with a slightly better FF of 0.30 lead to a power conversion efficiency of 0.81% (Table 3).

These preliminary results thus clearly show that the creation of an ICT by introduction of an electron-withdrawing group in the donor structure considerably improves the power conversion efficiency of the resulting bulk heterojunction due to the combined effects of extended photoresponse and increased V_{oc}.

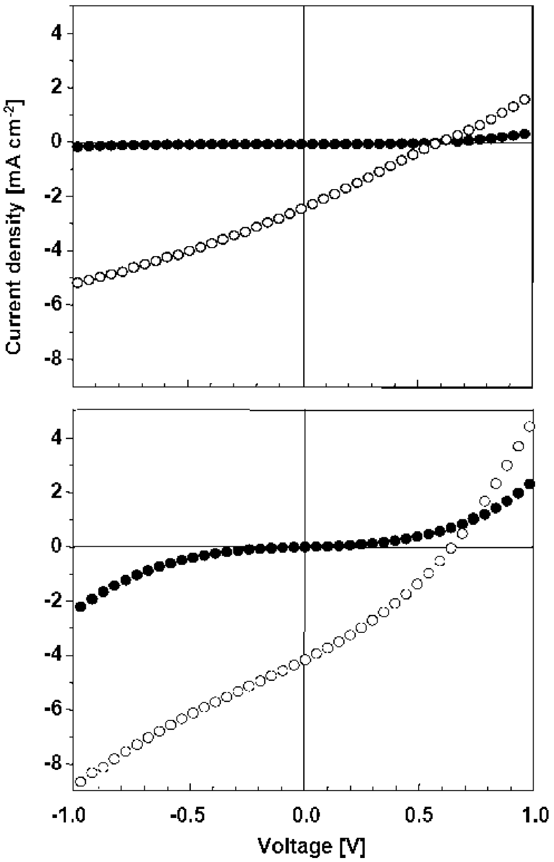

Figure 4. Current-density vs voltage curves of bulk heterojunctions of donors **1** (top) and **2** (bottom) and PCBM (ratio 1:3). In the dark (fillled circles) and under white light irradiation at 100 mW cm^{-2} (empty circles).

Table 3. Photovoltaic Characteristics of Bulk and Bilayer Heterojunctions Based on Donors **1**−**5** under AM 1.5 Simulated Solar Irradiation at 100 mW cm^{-2} Intensity

compd	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
1[a]	0.60	2.43	0.28	0.41
2[a]	0.66	4.10	0.30	0.81
1	0.48	2.33	0.41	0.46
3	0.72	1.97	0.34	0.49
4	0.89	3.65	0.36	1.17
5	0.96	3.65	0.29	1.02

[a] Bulk heterojunctions.

The photovoltaic properties of donors **1**, **3**, **4**, and **5** have been analyzed on bilayer heterojunction solar cells fabricated by successive thermal evaporation of 25 nm thick layers of donor and fullerene C_{60} followed by evaporation of a 60 nm thick aluminum electrode. Figure 5 shows the photocurrent action spectra of the cells based on the three compounds containing dicyanovinyl groups. For donor **3** the spectrum shows a first EQE maximum of 33% at 410 nm and a second maximum of 17% at 550 nm. Introduction of a second dicyanovinyl group in the donor structure (**4**) produces a decrease of EQE at 400 nm to 28% and an increase to ca. 20% around 550−570 nm. This trend is confirmed for the cell based on donor **5** for which EQE undergoes a further decrease around 400 nm and an increase around 550−600 nm, leading to a broad maximum of ∼28% in the 470−530 nm region.

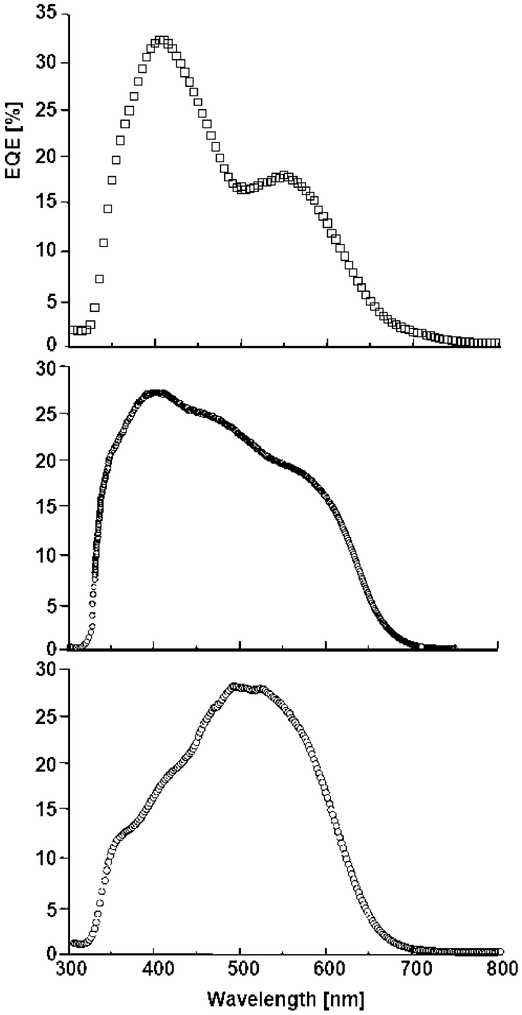

Figure 5. Photocurrent action spectra of bilayer heterojunctions of C_{60} and donors **3** (top) **4** (middle), and **5** (bottom) under monochromatic irradiation.

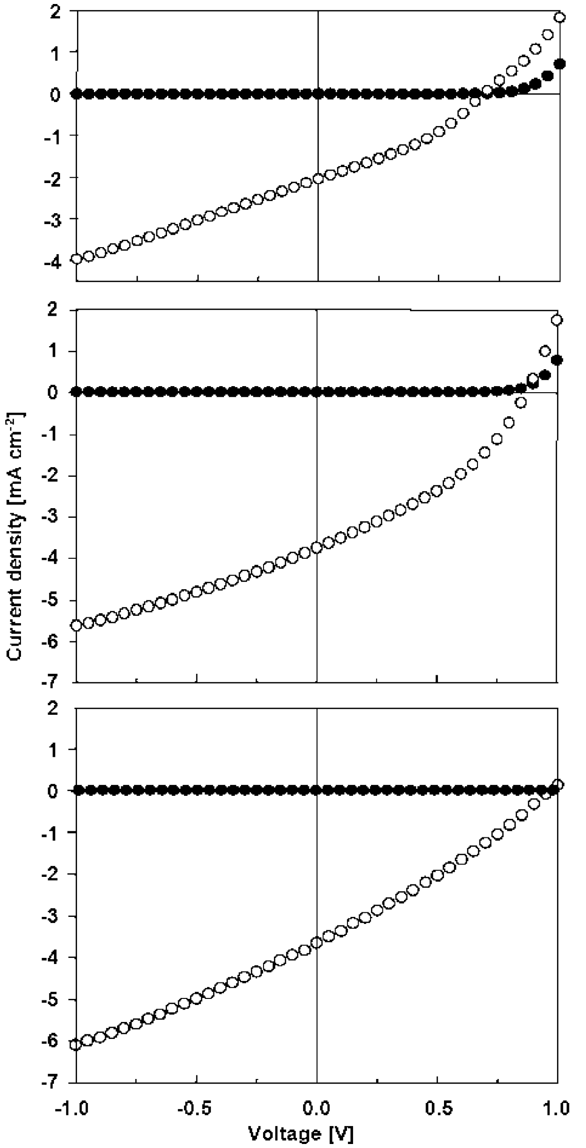

Figure 6. Current-density vs voltage curves of bilayer heterojunctions of C_{60} and donors **3** (top), **4** (middle), and **5** (bottom). In the dark (filled circles) and under simulated AM 1.5 solar irradiation at 100 mW cm^{-2} (empty circles).

As for bulk heterojunctions, comparison of the action spectra of the bilayer cells with the corresponding optical spectra in Figure 1 shows that the changes in the EQE spectrum are tightly correlated with the intensity of the ICT band in the absorption spectrum of the donor and hence with the number of acceptor groups in the structure. These results thus confirm that the creation of an ICT by introduction of acceptor groups in the donor structure is indeed effective for extending the photoresponse of the heterojunction solar cells.

Figure 6 shows the *J*/*V* curves of the three bilayer cells in the dark and under simulated AM 1.5 solar irradiation at a power intensity of 100 mW cm^{-2}. The curves recorded in the dark show a rectification behavior with an onset at ca. 0.80 V for compounds **3** and **4** and around 1.10 V for compound **5** (see Supporting Information).

The short-circuit current density increases from 1.97 mA cm^{-2} for compound **3** to 3.65 mA cm^{-2} for compounds **4** and **5**. The V_{oc} increases from 0.48 V for the reference donor **1** up to 0.963 V for compound **5**. This 0.48 V increase of V_{oc}, which nicely agrees with the 0.44 V higher $E°$ value for compound **5** (Table 2), clearly confirms the major influence of the oxidation potential of the donor on the V_{oc} of heterojunction solar cells.[22b] The power conversion efficiency η follows the same trend, although the highest value of 1.17% is obtained with donor **4** because of a better filling factor than for the cell based on donor **5**.

These results thus confirm that the introduction of electron-withdrawing groups in the donor structure leads to a considerable improvement of the power conversion efficiency of both bulk and bilayer heterojunction solar cells. To the best of our knowledge, except for the widely investigated phthalocyanines,[3,4,10] and pentacene,[30] the new donors reported here represent the first class of small molecules capable of leading to power conversion efficiencies better than 1%. Furthermore, having in mind that these first results have been obtained on devices of rather rudimentary technology, it seems reasonable to believe that they probably represent a minimum and that these new materials still have a significant margin of progress.

Conclusion

Amorphous donor materials based on star-shaped systems involving a TPA core derivatized with thienylenevinylene

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(30) Yoo, S.; Domerq, B.; Kippelen, B. *Appl. Phys. Lett.* **2004**, *85*, 5427.

conjugated branches and electron-withdrawing groups have been synthesized by a combination of Wittig−Horner and Knoevenagel reactions. Optical and electrochemical data have shown that introduction of electron-acceptor groups in the donor structure leads at the same time to an ICT and to a large increase of the oxidation potential.

Prototype bulk and bilayer heterojunctions solar cells have been fabricated using C_{60} derivatives as acceptor material. The action spectra of these devices under monochromatic irradiation show that the creation of an ICT by introduction of electron-withdrawing groups in the donor structure leads to a large increase of the maximum EQE to values exceeding 30% and to a considerable extension of the photoresponse toward longer wavelengths. The results obtained under AM 1.5 simulated solar irradiation show that the synergistic effects of extended photoresponse and increased open-circuit voltage lead to a significant improvement of the power conversion efficiency up to values close to 1.20%.

Although a detailed understanding of the influence of the ICT on the process of exciton diffusion and dissociation, charge recombination, and transport clearly requires detailed photophysical investigations, this first analysis of the structure−property relationships in a new family of donors provides a strong incitement to develop further work focused on both the design of donor systems based on the same approach and on the technological optimization of the devices.

Acknowledgment. We acknowledge financial support from the Region Pays de la Loire for the Ph.D. grant of S. R., SAMSUNG Company for financial support of part of this work, and SCAS of the University of Angers for analytical characterizations.

Supporting Information Available: Experimental procedure for the synthesis and characterization of all compounds. Experimental details for solar cell fabrication and characterization. UV−vis spectra of thin films of compounds **1**−**5** on glass. Photoluminescence emission spectra of compounds **3**, **4**, and **5** in toluene, dichorobenzene, and acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

JA058178E