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Small Molecular Donors for Organic Solar Cells Obtained by Simple and Clean Synthesis

Dora Demeter,^[a] Salma Mohamed,^[a] Andreea Diac,^[a, b] Ion Grosu,^[b] and Jean Roncali^{*,[a]}

A small donor–acceptor molecule is synthesized in a two-step procedure involving reaction of *N,N*-diphenylhydrazine on 2,5-diformylthiophene and Knoevenagel condensation. Results of UV/Vis absorption spectroscopy and cyclic voltammetry show that replacement of the phenyl ring bridge of a reference compound **2** by an azo group produces a slight red-shift of λ_{max} , an enhancement of the molecular absorption coefficient, and a decrease of the energy level of the frontier orbitals. A preliminary evaluation of the potentialities of compound **1** as donor material in a basic bilayer planar heterojunction cell of 28 mm² active area using C₆₀ as acceptor gave a short-circuit current density of 6.32 mA cm⁻² and a power conversion efficiency of 2.07%.

Organic photovoltaics (OPVs) are attracting increasing interest motivated by the technological opportunities offered by the lightness, plasticity, and flexibility of organic materials.^[1–6] However, besides scientific and technical interest, the considerable development of OPVs is mainly motivated by the expected drastic reductions of cost and environmental impact compared to the already established silicon solar cells.

In essence, designing an OPV cell involves the creation of a heterojunction by interfacing an electron donor material with an electron acceptor material.^[1] Soluble conjugated polymers constitute the main class of donor materials and high power conversion efficiencies (*PCEs*) of 8–9% have been reported for single-junction devices.^[2] However, the inherent polydispersity of polymers poses the problem of the reproducibility of the synthesis, purification, and, hence, composition and electronic properties of the active material. An alternative approach consists in replacement of the polymers by molecular donors. Molecular donors have been used in multilayer planar heterojunction (PHJ) cells fabricated by vacuum deposition for a long time, and the field is still very active.^[3] Soluble molecular donors introduced in 2005 in the fabrication of solution-processed bulk heterojunction (BHJ) solar cells^[4] have rapidly gained considerable interest and given rise to the synthesis of a huge number of new chromophores.^[5] The field has

witnessed rapid progress and solution-processed BHJ cells with *PCE* values comparable to those obtained with the best polymer-based devices have been recently reported by several groups.^[6] However, these high performances have been obtained with complex molecules of high molecular weight, prepared by multistep syntheses involving metal-catalyzed coupling reactions and with overall yields sometimes limited to a few percents.

In addition to problems of the cost of the synthesis, the presence of remnant traces of metals such as palladium or nickel can have deleterious effects on the performances of organic semi-conductors.^[7] Recently, several authors have discussed issues associated with the industrial development of OPV and emphasized the key role of the cost, scalability, and environmental impact of the synthesis of active material.^[8] In this context, our group has undertaken a project aimed at a drastic reduction of the size and complexity of molecular donors.^[9,10] This approach is expected to contribute to decrease the cost of active OPV materials by improving the overall yield and scalability of the synthesis and to limit its environmental impact by reducing the number of synthetic steps and avoid as much as possible, the use of metal-catalysts.

In recent years several groups have described efficient OPV cells fabricated by vacuum-deposition of small molecular donors. Thus, Würthner et al. have reported cells with *PCE* of 6.10% based on merocyanines donors.^[11] Wong et al. have synthesized donor–acceptor molecules based on triphenylamine and fabricated solar cells with a maximum *PCE* of 6.80% using C₇₀ as acceptor.^[12]

We have recently described a cell of 4.0% *PCE* fabricated by co-evaporation of compound **2** (Scheme 1) and C₆₀ as acceptor.^[9–ab,13] Furthermore, an even a smaller molecule such as compound **3** can still produce a short-circuit current density (J_{sc}) of almost 7.0 mA cm⁻² and a *PCE* close to 2.0%.^[10b] However the light-harvesting properties of this molecule are limited ($\lambda_{\text{max}} = 473$ nm, $\lambda_{\text{onset}} = 550$ nm).

Grazulevicius et al. have widely developed hole-transporting materials synthesized by condensation of diarylhydrazines with various aldehydes.^[14] More recently this approach was used by Shen et al. for the synthesis of sensitizers for dye-sensitized solar cells (DSSCs).^[15] As

Scheme 1. Chemical structure of the target donor **1** and reference compounds.

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a further step in the development of donor molecules for OPV combining simplicity, low molecular weight, and clean synthesis we report here the preparation of compound (**1**) with a diphenylhydrazone donor block and a preliminary evaluation of its potentialities as donor in basic bilayer PHJ cells.

The synthesis of compound **1** is depicted in Scheme 2. Shen et al. have synthesized sensitizers by a three-step synthesis involving reaction of *N,N*-diphenylhydrazine with 2-thiophene carboxaldehyde followed by formylation of the free α -position

Scheme 2. Synthesis of the target compound **1**.

of thiophene of the resulting hydrazone and condensation with cyanoacrylic acid.^[15] In an attempt to simplify the synthesis by skipping the formylation step, we have directly reacted *N,N*-diphenylhydrazine (**7**) with 2,5-thiophene dicarboxaldehyde (**6**). Reaction of **6** with one equivalent of **7** in methanol at low temperature gives as major product the bis-adduct **5** while the target monoaldehyde **4** was isolated in 12% yield. In a second series of experiments, one equivalent of **7** was reacted with 0.5 equivalent of dialdehyde **6** using a more dilute reaction medium. Under these conditions aldehyde **4** was isolated in 62% yield together with 21% of the bis-adduct **5** while 18% of the starting dialdehyde **6** were recovered. A Knoevenagel condensation of aldehyde **4** and malonodinitrile gave the target compound **1** in 70% yield (Scheme 2).

The UV/Vis absorption spectrum of compound **1** in methylene chloride shows an absorption maximum (λ_{max}) at 504 nm (Figure 1), which corresponds to a 31 nm bathochromic shift compared to compound **3** and a 3 nm red-shift compared to compound **2**. Compound **1** shows a good solubility in chloroform (25 mg mL⁻¹) and in chlorobenzene although the solubility is lower in this solvent (12.5 mg mL⁻¹). The UV/Vis absorption spectra of thin-films cast on glass from solutions in these two solvents show in both cases a bathochromic shift of λ_{max} to ca. 525 nm and a broadening of the absorption band due to intermolecular interactions in the solid state.

A cyclic voltammogram (CV) of **1** recorded in CH₂Cl₂ with Bu₄NPF₆ as supporting electrolyte is shown in Figure 2. This CV exhibits a quasi-irreversible oxidation wave with an anodic peak potential (E_{pa}) at 1.32 V. The weak cathodic peak observed around 1.0 V in the reverse scan suggests the formation of

Figure 1. Top: UV/Vis absorption spectrum of compound **1** in methylene chloride. Bottom: normalized UV/Vis absorption spectra of thin films of compound **1** spun-cast on glass from chloroform solution (dashed line) and chlorobenzene solution (solid line).

Figure 2. Cyclic voltammogram of compound **1** in 0.10 M Bu₄NPF₆/CH₂Cl₂, Pt electrodes, scan rate 100 mV s⁻¹.

a more extended conjugated system by coupling of the cation radical, as frequently observed in the electrochemistry of TPA derivatives.^[16] In the negative potential region (not shown), the CV shows an irreversible reduction wave peaking at -0.91 V indicative of unstable anion radical. Comparison of the data for compound **1** to those for **2** and **3** shows that compound **1** presents the most red-shifted λ_{max} , the highest molecular absorption coefficient (ϵ), and the lowest highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (Table 1). Considering the fact that the open-circuit voltage (V_{oc}) of OPV cells depends on the difference between the LUMO of the acceptor and the HOMO of the donor, this deep HOMO level appears interesting.^[17] These results show that replacement of the phenyl bridge of compound **2** by an azo group produces interesting modifications of the electronic properties of the molecule regarding a possible use as donor in OPV cells. It is worth noting that these modifications are associated with a decrease of the molecular

Table 1. Data of UV/Vis spectroscopy and cyclic voltammetry in the conditions of Figures 1 and 2.

Donor	MW [g mol ⁻¹]	λ_{max} [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]	E_{pa} [V]	E_{pc} [V]	$E_{\text{HOMO}}^{[a]}$ [eV]	E_{LUMO} [eV]
1	354	504	39 000	1.32	-0.91	-6.20	-4.35
2 ^[b]	403	501	33 900	1.01	-1.23	-5.89	-4.06
3 ^[c]	327	473	27 000	1.20	-1.17	-6.08	-4.12

[a] Using an offset of -4.99 eV for SCE vs. the vacuum level.^[18] [b] From Ref. [9a]. [c] From Ref. [10b].

weight and a simplification of the synthesis with in particular the elimination of the Stille coupling involved in the synthesis of compound 2.^[9]

A preliminary evaluation of potentialities of compound 1 as donor for OPV has been carried out on bilayer PHJ cells fabricated by spin-casting a ca. 20 nm thick film of 1 from a chloroform solution onto indium tin oxide (ITO) substrates precoated with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The substrates were then introduced into a vacuum chamber, a 30 nm thick layer of C₆₀ or C₇₀ fullerene acceptor was deposited by thermal evaporation under a pressure of 2 × 10⁻⁶ mbar, and the devices were completed by deposition of a 100 nm layer of aluminum. Although the solubility of compound 1 could allow the fabrication of solution-processed BHJ cells, no attempt at that direction was made at this stage. In fact BHJ cells generally require tedious optimization work whereas simple PHJ cells, although less efficient, are more suitable for a first evaluation of new materials as they give more reproducible and more reliable results.

As shown in Table 2, as-fabricated cells show short-circuit current densities (J_{sc}) in the range of 2.50 to 3.50 mA cm⁻² and *PCE* of 0.60 to 0.80%. Devices containing C₇₀ as acceptor give slightly better J_{sc} and *PCE* values but lower fill factors (*FF*). Application of a 10 min thermal treatment at 100 °C strongly improves the photovoltaic characteristics with in particular a large increase of J_{sc} to values exceeding 6.00 mA cm⁻². After annealing, the best results are obtained with C₆₀. Although we

Table 2. Photovoltaic characteristics of 1/acceptor bilayer solar cells under AM 1.5 simulated solar light with an incident power light of 90 mW cm⁻².

Cell	Acceptor	Ann. temp [°C]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	<i>FF</i> [%]	<i>PCE</i> [%]
1	C ₆₀	ambient	2.48	0.84	27.4	0.63
2	C ₆₀	ambient	2.05	0.89	28.1	0.57
3	C ₇₀	ambient	3.17	0.86	23.9	0.72
4	C ₇₀	ambient	3.46	0.88	25.5	0.85
1	C ₆₀	100	6.32	0.79	37.4	2.07
2	C ₆₀	100	5.72	0.82	35.3	1.83
3	C ₇₀	100	4.64	0.87	29.3	1.31
4	C ₇₀	100	4.16	0.89	29.1	1.19
1	C ₆₀	110	6.40	0.75	33.1	1.76
2	C ₆₀	110	6.50	0.64	37.3	1.72
3	C ₇₀	110	4.73	0.77	27.9	1.13
4	C ₇₀	110	5.27	0.77	27.4	1.23

have no explanation for this phenomenon it can be hypothesized that the thermally-induced rearrangement of the active donor/acceptor (D/A) interfacial zone is different for the two acceptors. Application of higher annealing temperature (110 °C) produces a small further increase of J_{sc} but begins to deteriorate V_{oc} and *FF* values. Figure 3 shows the *J-V* curves for the best device of the series, which gave a J_{sc} of 6.32 mA cm⁻², a V_{oc} of 0.79 V, and a *PCE* of 2.07%.

Figure 3. a) Current density–voltage curves for a bilayer solar cell (ITO/PEDOT:PSS/1/C₆₀/aluminium). In the dark (open circles) and under simulated solar light with incident power light of 90 mW cm⁻² (black circles). b) External quantum efficiency spectra of the bilayer cells 1/C₆₀.

Figure 3 (bottom) shows the external quantum efficiency (EQE) action spectrum of the best device under monochromatic irradiation. The spectrum shows a broad maximum of ca. 55–60% in the 400–600 nm region with an onset of photocurrent at ca. 620 nm. Although these results are encouraging they also underline the need for improving the light-harvesting properties of the donor by further structural modification.

When evaluated in the above conditions, reference compound 2 gives a *PCE* of 2.50%. In a recently published paper, a thorough optimization of the device architecture has allowed to increase this value to 4.00% for cells based on co-evaporated bulk heterojunction of donor and C₆₀ layer.^[13] This result suggests that there is still room for improvement in the case of donor 1.

To summarize, a soluble push–pull molecule has been synthesized using two condensation reactions with water as by-product. Comparison of the electronic properties to those of a reference compound shows that replacement of thiophene

by an azo bridge leads at the same time to a decrease of molecular weight and to improved optical properties and energy levels a priori favorable for photovoltaic conversion. Preliminary tests with simple bilayer solar cells show that performances comparable to those reported for much larger molecules evaluated in optimized devices of smaller active area can be obtained with a small molecule obtained by simple and clean chemistry.

Work aiming at the extension of this synthetic approach with in particular optimization of the selectivity of the reaction of diphenylhydrazine with dialdehydes, the design of molecules with improved light-harvesting properties, and further evaluation in BHJ cells is now underway and will be reported in future publications

Experimental Section

General

NMR spectra were recorded with a Bruker AVANCE III 300 (^1H , 300 MHz and ^{13}C , 75 MHz) or Bruker AVANCE DRX 500 (^1H , 500 MHz and ^{13}C , 125 MHz). Chemical shifts are given in ppm relative to TMS. Infrared spectra were recorded on a Bruker spectrometer Vertex 70 and UV/Vis spectra with a Perkin–Elmer Lambda 19 or 950 spectrometer. Melting points are uncorrected. Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer using dithranol as matrix. Cyclic voltammetry was performed in dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.10 M as supporting electrolyte) was purchased from Acros and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment. Experiments were carried out in a one-compartment cell equipped with platinum electrodes and saturated calomel reference electrode (SCE) with a Bio-logic SP-150 potentiostat with positive feedback compensation.

Synthesis

5-((2,2-diphenylhydrazono)methyl)thiophene-2-carbaldehyde (**4**). A solution of thiophene-2,5-dicarbaldehyde (**6**) (1.27 g, 9.06 mmol) in 50 mL of dry THF is added dropwise to a mixture of *N,N*-diphenylhydrazine hydrochloride (**7**) (1.0 g, 4.53 mmol) and sodium acetate (1.40 g, 18.12 mmol) in 15 mL of dry methanol under argon atmosphere at room temperature. The reaction mixture is stirred overnight at room temperature and then diluted with methylene chloride, washed with water and brine. After removal of the solvent the residue is chromatographed on silica gel using methylene chloride as eluent to afford a yellow powder (0.85 g, 62%). ^1H NMR (300 MHz, CDCl_3): δ = 9.85 (s, 1H), 7.61 (d, 1H, J = 3.9 Hz), 7.47–7.42 (m, 5H), 7.27–7.18 (m, 6H), 6.19 ppm (d, 1H, J = 3.9 Hz). MALDI-TOF: 306.2.

(*E*)-2-((2,2-diphenylhydrazono)methyl)thiophen-2-yl)methylene)malononitrile (**1**) Aldehyde **4** 150 mg (0.45 mmol) was dissolved in 15 mL of chloroform, malononitrile (60 mg, 0.9 mmol, 2 equiv) and one drop of triethylamine were added. The mixture was refluxed for two hours. The solvent was evaporated and the product was purified by column chromatography on silica gel (eluting with dichloromethane), yielding a yellow powder (0.12 g, 0.316 mmol, 70%). ^1H NMR (300 MHz, CDCl_3): δ = 7.70 (s, 1H), 7.62 (d, 1H, J = 3.9 Hz), 7.48–7.43 (m, 4H), 7.29–7.27 (d, 2H, J = 7.5 Hz) 7.20–7.17 (m, 5H), 7.01 ppm (d, 1H, J = 3.9 Hz). ^{13}C NMR (75 MHz, CDCl_3): δ =

153.8, 150.0, 142.3, 139.1, 133.8, 130.0, 127.3, 126.4, 125.8, 122.5, 122.4, 114.5, 113.5, 75.7 ppm. MS MALDI-TOF: 354.2.

Device fabrication and testing

Indium-tin oxide coated glass slides of 24 mm $\times$ 25 mm $\times$ 1.1 mm dimensions with a surface resistance of 10 $\Omega/\square$ were purchased from Kintec company. Part of the ITO layer was etched away with 37% HCl. The ITO electrodes were then cleaned in ultrasonic bath (successively Deconex (from VWR international GmbH), distilled water (15.3 $\text{M}\Omega\text{cm}^{-1}$), acetone, ethanol and distilled water again for 10 min each and dried in an oven at 100 $^\circ\text{C}$. The dried electrodes were then modified by a spun-cast layer of PEDOT:PSS (Clevios P VP. Al 4083 (HC-Starck) filtered through a 0.45 μm membrane just prior use). Spin-casting was achieved at 5000 rpm (r = 10 s, t = 60 s), and the electrode was then dried at 130 $^\circ\text{C}$ for 15 min. Films of donor materials (ca 20 nm) were spun-cast in atmospheric conditions from chloroform solutions containing 4 mg donor/mL. After film deposition the devices were introduced in an argon glovebox (200B, MBraun) equipped with a vacuum chamber and a 25 nm film of Fullerene C_{60} (99+%) (MER Corporation) and a 100 nm thick aluminium electrode were thermally evaporated on top of the donor film under a pressure of 2×10^{-6} mbar through a mask defining two cells of 6.0 mm diameter (0.28 cm^2) on each ITO electrode.

The J vs V curves of the devices were recorded in the dark and under illumination using a Keithley 236 source-measure unit and a home-made acquisition program. The light source was an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttechnik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). The devices were illuminated through the ITO electrode side. The efficiency values reported here are not corrected for the possible spectral mismatch of the solar simulator. External quantum efficiency (EQE) was measured using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (PerkinElmer 7225) and a S2281 photodiode (Hamamatsu).

Keywords: condensations • donor–acceptor • energy conversion • photovoltaics • solar cells

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COMMUNICATIONS

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Small Molecular Donors for Organic Solar Cells Obtained by Simple and Clean Synthesis

Keep it simple: A simple donor–acceptor molecule is synthesized from 2,5-thiophene dialdehyde using two condensation reactions with water as sole by-product. A 30 mm^2 simple bilayer solar cell fabricated with a spun-cast film of donor and vacuum-deposited C_{60} shows a power conversion efficiency $> 2.0\%$ under simulated solar light.