

# A star-shaped triphenylamine $\pi$ -conjugated system with internal charge-transfer as donor material for hetero-junction solar cells†

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**Introduction of dicyanovinyl groups on a triphenylamine-based conjugated system leads to an intramolecular charge transfer which extends the spectral response and raises the open-circuit voltage of the resulting hetero-junction solar cells.**

Organic solar cells are a focus of considerable research effort motivated by the perspective of achieving low-cost, lightweight and flexible power sources.<sup>1–8</sup> Bulk hetero-junctions based on interpenetrated networks of  $\pi$ -conjugated polymers and soluble  $C_{60}$  derivatives have been intensively investigated in the past decade and power conversion efficiencies in the 4–5% range have been recently reported.<sup>5,6</sup> In parallel, significant progress has been also accomplished in multi-layer hetero-junctions based on small molecules<sup>7–11</sup> and efficiencies in the 3–4% range have been published.<sup>9,10</sup>

Low dimensional  $\pi$ -conjugated systems such as *e.g.* oligothiophenes lead to organic semi-conductors with highly anisotropic electrical and optical properties,<sup>11–15</sup> which poses specific problem for device fabrication. Thus, whereas a vertical orientation of the conjugated chains on the substrate is known to improve mobility in organic field-effect transistors,<sup>12–14</sup> such an orientation is detrimental for solar cells as it strongly reduces the absorption of the incident light as well as hole transport to the electrodes.<sup>11,15,16</sup>

Organic glasses derived from triphenylamine (TPA)-based compounds have been widely investigated as active material for hole transport and electroluminescence.<sup>17</sup> Whereas the amorphous character of these materials offers possibilities to develop active materials for solar cells with isotropic optical and charge-transport properties, the use of TPA-based materials for photovoltaic conversion has been scarcely considered. Shirota and co-workers have used TPA-based starburst molecules containing nitro or dimethylboryl acceptor groups as donor in bilayer hetero-junctions. However, the conversion efficiency of these cells was limited to 0.4 and 0.1% respectively under monochromatic irradiation in the absorption band of the donor ( $\sim 440$  nm).<sup>17b</sup>

We now report preliminary results on a star-shaped tris[4-(2-thienyl)phenyl]amine core modified by peripheral electron-withdrawing dicyanovinyl groups (**1**) and its use as donor material for the realization of hetero-junction solar cells. We show that the creation of an intramolecular charge-transfer (ICT) leads simultaneously to an extension of the spectral response and to an increase of the open-circuit voltage of the resulting solar cells.

The synthesis of compound **1** is depicted in Scheme 1. A Stille coupling of the commercially available tribromotriphenylamine **4** with the stannyl derivative of thiophene gave tris[4-(2-thienyl)phenyl]amine **3**<sup>18</sup> in 85% yield. Vilsmeier formylation of compound **3** gave tricarboxaldehyde **2** in 90% yield. Knoevenagel condensation of compound **2** with malononitrile gave the target molecule tris(4-(5-dicyanomethylidenemethyl-2-thienyl)phenyl)amine **1** in 76% yield.†

The cyclic voltammogram of compound **1** shows a reversible anodic wave peaking at 1.09 V vs Ag/AgCl (Fig. 1). This high value shows that the electron-withdrawing dicyanovinyl groups induce a large increase of the oxidation potential compared to compound **3** ( $E_{pa} = 0.51$  V vs Ag/AgCl).<sup>18</sup> Furthermore, the stability of the cation radical indicated by the reversibility of the oxidation process appears as a positive fact for the use of the corresponding material for hole transport.

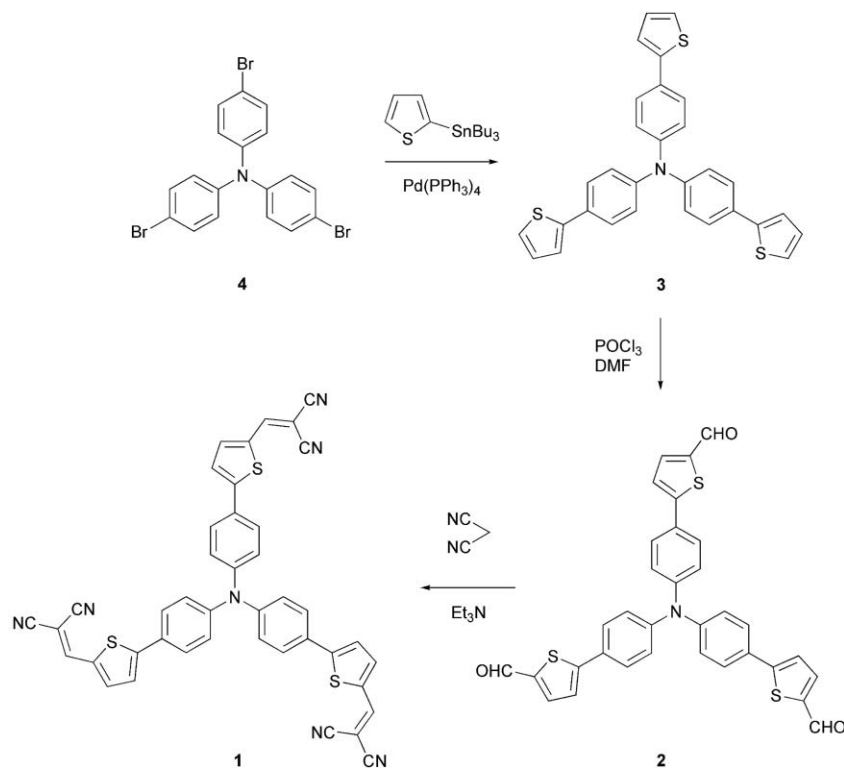
The UV-Vis spectrum of compound **1** in  $CH_2Cl_2$  shows a first absorption band with a  $\lambda_{max}$  at 368 nm and a second more intense band with  $\lambda_{max}$  at 510 nm (Fig. 2). Based on the  $\lambda_{max}$  of compound **3** (366 nm),<sup>18</sup> the first absorption band can be assigned to a  $\pi$ - $\pi^*$  transition and the main absorption band at 510 nm to an ICT between the donor and acceptor parts of the molecule. The optical spectrum of a thin film of **1** thermally evaporated on glass exhibits a  $\lambda_{max}$  at 545 nm and a red shift of the absorption onset to  $\sim 680$  nm. (Fig. 3 and ESI†). These large shifts suggest the occurrence of strong intermolecular interactions in the solid state. The low energy absorption edge of the spectrum leads to a band gap  $E_g$  of  $\sim 1.80$  eV. Powder X-ray diffraction spectra of the films did not show any peak, confirming that compound **1** is amorphous similarly to many TPA derivatives.<sup>17</sup>

Hetero-junction solar cells of 6 mm diameter have been realized on ITO substrates spin-coated with a 60 nm film of Baytron P<sup>®</sup>. Layers of donor **1** and  $C_{60}$  fullerene as acceptor of  $\sim 25$  nm thickness were successively grown by thermal evaporation under vacuum and the devices were completed by deposition of a 60 nm thick aluminium top electrode.

As shown in Fig. 3, the UV-Vis absorption spectrum of the bilayer is more or less the sum of the spectra of the two components. The spectrum shows a first intense band with  $\lambda_{max}$  at ca 350 nm corresponding to the absorption of  $C_{60}$  and to the first absorption band of compound **1** and a second broad band with  $\lambda_{max}$  at 520 nm. The apparent blue shift of the ICT band of **1** in the spectrum of the bilayer is due to the convolution with the  $C_{60}$  absorption shoulder around 450 nm. The photo-current action spectrum recorded under monochromatic irradiation shows that the incident photon conversion efficiency (IPCE) presents a first shoulder around 350 nm and a broad maximum of ca 28% in the

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† Electronic supplementary information (ESI) available: current voltage curve of the cell ITO/I(25nm)/ $C_{60}$ (25nm)/Al(60nm) and electronic absorption spectrum of a film of **1** evaporated on glass. See DOI: 10.1039/b516781g



Scheme 1

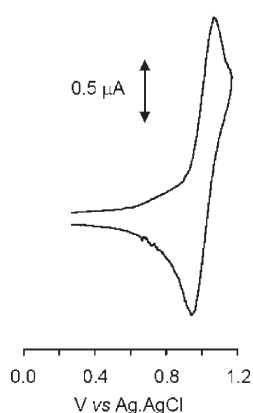


Fig. 1 Cyclic voltammogram of compound **1** ( $ca\ 10^{-4}$  M) in 0.10 M  $Bu_4NPF_6/CH_2Cl_2$  scan rate  $100\text{ mV s}^{-1}$ .

470–540 nm region. The onset of the photo-current at  $\sim 700$  nm shows that the ICT in compound **1** effectively extends the spectral response of the hetero-junction.

Fig. 4 shows the current density-voltage ( $J$ - $V$ ) characteristics of the cell in the dark and under simulated AM 1.5 solar illumination at  $100\text{ mW cm}^{-2}$  light intensity. The curve recorded in the dark shows a rectification behaviour at  $ca.\ 1.70$  V with a current onset around 1.20 V (see ESI†). Under illumination the cell delivers a short-circuit current density ( $J_{sc}$ ) of  $3.65\text{ mA cm}^{-2}$ . The  $J$ - $V$  curves show a persistent slope at negative voltages which can be attributed to various causes such as high series resistance, electron-hole recombination, low shunt resistance or photoconductivity. Further work is needed to clarify this point.

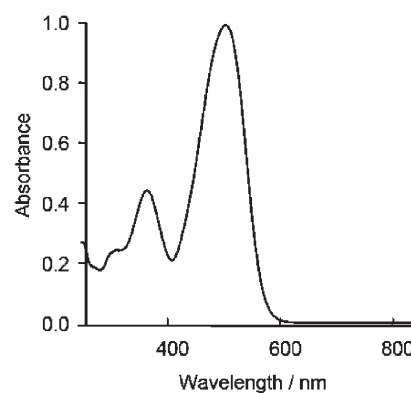
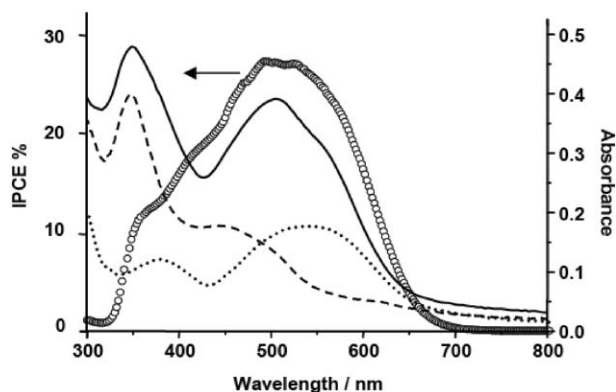


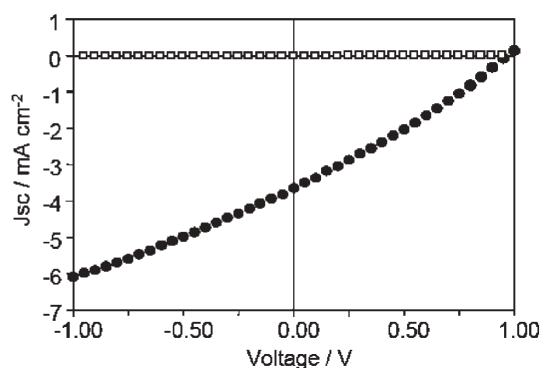
Fig. 2 UV-Vis absorption spectrum of compound **1** in  $CH_2Cl_2$ .

The cell presents an open-circuit voltage ( $V_{oc}$ ) of 0.963 V. This high value can be related to the high oxidation potential of **1**.<sup>19,20</sup> Combined with a rather low filling factor of 0.29, these  $J_{sc}$  and  $V_{oc}$  values lead to a power conversion efficiency of 1.02%.

To summarize we have shown that the introduction of peripheral dicyanovinyl acceptor groups on a tris[4-(2-thienyl)phenyl]amine leads simultaneously to an extension of the absorption towards longer wavelengths and to an increase of the oxidation potential. Preliminary results on prototype bi-layer hetero-junction solar cells confirm that this type of donor material allows extended spectral response, high open-circuit voltage and very promising power conversion efficiency to be combined. Although a detailed understanding of the consequences of ICT on exciton dissociation, charge recombination and transport clearly requires further work and, in particular, detailed photo-physical studies, these first results clearly provide a strong inducement to



**Fig. 3** UV-vis absorption spectra of 25 nm films of  $C_{60}$  (dashed line), compound **1** (dotted line) bilayer (solid line) and EQE under monochromatic irradiation (empty circles).



**Fig. 4**  $J$ - $V$  curves of ITO/Baytron1/ $C_{60}$ /Al devices recorded in the dark (empty squares) and under  $100 \text{ mW cm}^{-2}$  white light illumination (black circles).

synthesize new donor materials designed according to the same concept and to extend the evaluation of these materials to other type of solar cells such as bulk hetero-junctions. Work in these directions is now underway.

## Notes and references

‡ M.p.  $325^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.79 (s, 1H), 7.71 (d, 1H,  $^3J = 4.13\text{Hz}$ ), 7.64 (d, 2H,  $^3J = 8.69\text{Hz}$ ), 7.41 (d, 1H,  $^3J = 4.09\text{Hz}$ ), 7.20 (d, 2H,  $^3J = 8.69\text{Hz}$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) (155.6, 150.4, 147.8, 140.2, 133.9, 128.0, 127.8, 124.8, 124.1, 114.2, 113.4, 76.3. IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2220 ( $\text{C}\equiv\text{N}$ ), UV-vis  $\lambda_{\text{max}}$  nm (log $\epsilon$ ) 368, 509 (5.1). MS MALDI-TOF  $\text{C}_{42}\text{H}_{21}\text{N}_7\text{S}_3$  719 M.<sup>+</sup>

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