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Triphenylamine/Tetracyanobutadiene-Based D-A-D π-Conjugated Systems as Molecular Donors for Organic Solar Cells

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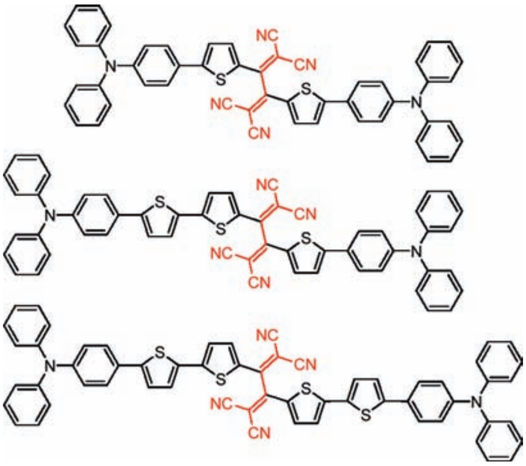
ABSTRACT



Thiophene-based D-A-D π-conjugated systems containing triphenylamine end groups connected to a 1,1,4,4-tetracyanobuta-1,3-diene acceptor by oligothiophene chains of variable length have been synthesized. These compounds show interesting light-harvesting properties and low-lying HOMO levels. Preliminary results on bilayer heterojunction solar cells with C_{60} as acceptor show power conversion efficiency higher than 1.0%.

Small π-conjugated molecules have represented a major class of active materials in organic solar cells (OSCs) during the early developments of the field.[1]

Although the past decade has been marked by the tremendous development of bulk heterojunction (BHJ) cells based on conjugated polymers, molecular donors have remained a focus of high interest not only for the fabrication of vacuum-deposited bilayer heterojunctions[2] but more recently as donor materials for the realization of solution-processed BHJ solar cells.[3]

In this context, an interesting approach consists of the design of molecular donors in which an internal charge transfer is created by the introduction of electron acceptor (A) groups in the structure of the donor.[4]

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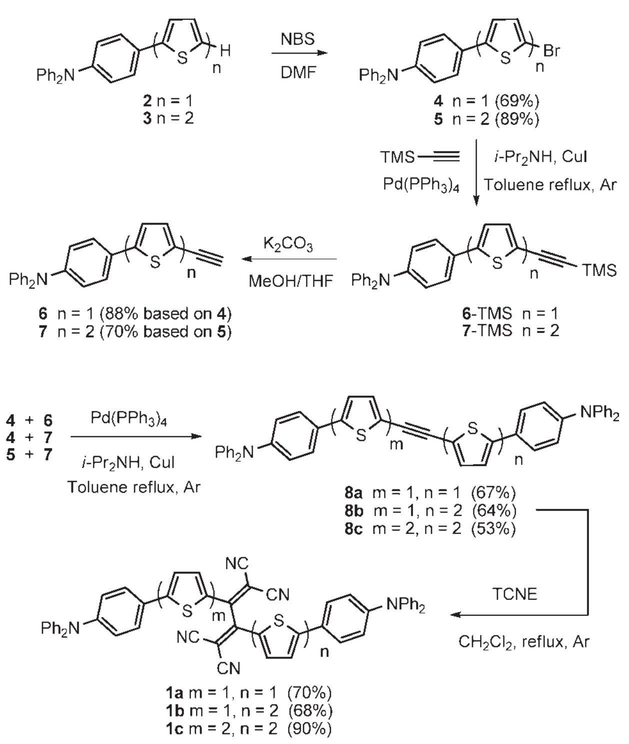
In recent years, this approach has led to the synthesis of different classes of active molecules.[3−17] In particular, symmetrical D-A-D or A-D-A systems have been shown to lead to interesting photovoltaic performances in both vacuum-deposited planar heterojunction and solution-processed bulk heterojunction OSCs.

Thus, a large variety of donor materials have been designed by combining donor blocks D, essentially derived from oligothiophenes or triphenylamine (TPA), with electron-acceptor moieties A such as dicyanovinyl,[4,9] dicyanomethylenepyrane,[10] fluorenone,[11] squaraine,[12] diketopyrrolopyrrole,[13] indigo,[14] benzothiadiazole,[15,16] or borondipyrromethene.[17]

Scheme 1. Synthesis of Molecules **1**



1,1,4,4-Tetracyanobuta-1,3-diene (TCBD) has been developed as an electron-accepting group for the synthesis of D-π-A push−pull chromophores with enhanced NLO properties and improved thermal stability.[18] We report here on the synthesis and the electronic properties of symmetrical and unsymmetrical D-π-A-π-D molecules **1** using TCBD as acceptor and oligothienyl-TPA chains as donor blocks together with preliminary results on the potentialities of these compounds in OSCs.

The synthesis of the target compounds **1** is shown in Scheme 1. Regioselective monobromination of TPA-derivatized-thiophene and 2,2′-bithiophene **2** and **3**[19] by NBS, gave the bromo compounds **4** and **5**, respectively. Sonogashira reaction of trimethylsilylacetylene with **4** and **5** followed by elimination of the trimethylsilyl group gave the acetylenic compounds **6** and **7**. These latter compounds were subjected to another Sonogashira coupling with bromo compounds **4** or **5** in the presence of CuI and $Pd(PPh_3)_4$ as catalyst to give the symmetrical (**8a**, **8c**) and unsymmetrical (**8b**) compounds. Reaction of compounds **8** with tetracyanoethylene (TCNE) led to the target molecules **1a**−**c** in 68−90% yield after purification by chromatography.

This latter reaction is highly efficient for introducing a strong electron acceptor such as TCBD in place of an acetylenic bond[20] as illustrated by the synthesis of TPA[21] and oligothiophene[22] derivatives.

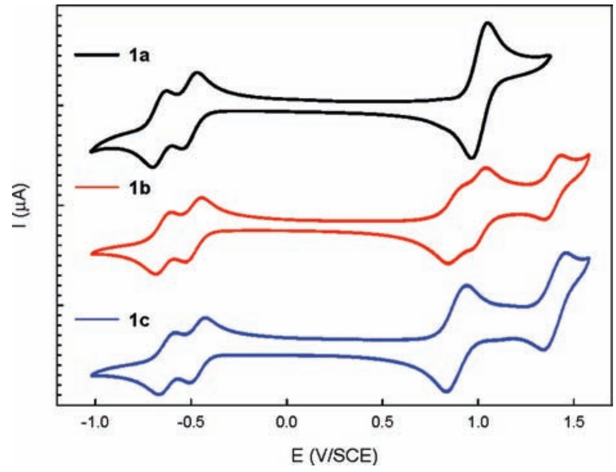


Figure 1. CVs of 0.5 mM solutions of compounds **1** in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrode, scan rate = 100 mV/s.

The electronic properties of compounds **1** have been analyzed by cyclic voltammetry (CV) and UV−vis absorption spectroscopy. The CV of **1a** (Figure 1) exhibits a two-electron reversible oxidation wave with anodic peak potential E_{pa}^1 at 1.05 V assigned to the simultaneous oxidation of the two thienyl-TPA branches. The CV shows also

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Table 1. Electrochemical, Optical, and Thermal Data for Compounds **1**

compd	$E_{pr}{}^{2}$/V^{a}	$E_{pr}{}^{1}$/V^{a}	$E_{pa}{}^{1}$/V^{a}	$E_{pa}{}^{2}$/V^{a}	$E_{pa}{}^{3}$/V^{a}	λ_{max} (ICT)/nm (ε/M^{-1}cm^{-1})^{b}	ΔE_{elec} (eV)^{c}	ΔE_{opt} (eV)^{d}	T/°C^{e}
1a	−0.71	−0.55	1.05			569 (46600)	1.53	2.18	375
1b	−0.68	−0.53	0.93	1.05	1.44	576 (57400)	1.38	2.15	165
1c	−0.67	−0.50	0.94	1.44		586 (61600)	1.37	2.12	208

[a] Performed with 0.5 mM of compound in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrode, SCE reference, scan rate = 100 mV/s. [b] In CH_2Cl_2. [c] Estimated from the difference between standard potentials of the first electrochemical oxidation and reduction waves. [d] Estimated from λ_{max} (ICT). [e] Temperature corresponding to 5% weight loss obtained from TGA analysis under N_2 with a heating rate of 10 °C/min.

two successive one-electron reduction waves at -0.55 V ($E_{pr}{}^{1}$) and -0.71 V ($E_{pr}{}^{2}$) associated to the reduction of the central TCBD. $E_{pa}{}^{1}$ is positively shifted by 220 mV compared to **8a** due to the $-M$ and $-I$ effects of the TCBD block (Table S1, Supporting Information).

The lengthening of the oligothiophene chain in **1b** and **1c** induces a negative shift of $E_{pa}{}^{1}$ together with the appearance of additional oxidation peaks at more positive potential (Figure 1 and Table 1). Thus, the CV of the unsymmetrical compound **1b** shows three one-electron reversible oxidation waves peaking at 0.93, 1.04, and 1.44 V. The first and the second processes are assigned to the successive oxidation of the bithienyl- and thienyl-TPA branches in cation radical whereas the third one can be related to the oxidation of the bithienyl-TPA branch to the dication state. This assignment is consistent with the CV of **1c**, which shows two two-electron reversible oxidation peaks at $E_{pa}{}^{1}$ = 0.94 V and $E_{pa}{}^{2}$ = 1.44 V corresponding to the successive formation of the cation radical and dication of the two bithienyl-TPA branches.

These E_{pa} values show that the lateral branches are rather electronically independent suggesting that the central TCBD interrupts the conjugation. This interpretation is further supported by the limited positive shift observed in the first reduction potential between **1a** and **1c**.

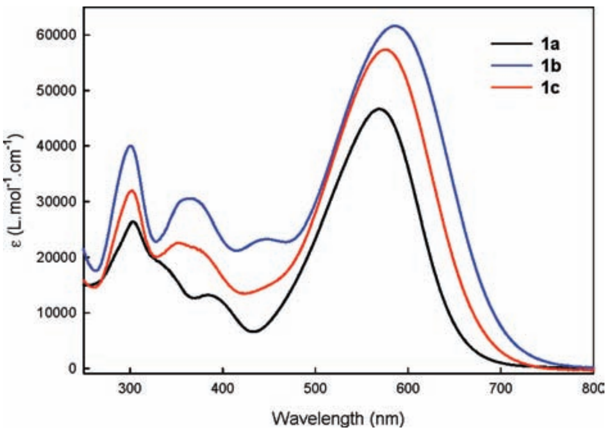

Figure 2. Absorption spectra of compounds **1** in CH_2Cl_2.

The UV−vis absorption spectra of compounds **1** in CH_2Cl_2 show a broad ICT band extending from 450 to 700 nm with relatively high molar extinction coefficients ε (Figure 2 and Table 1). The extension of the conjugated branches from **1a** to **1c** leads to a 17 nm bathochromic shift of λ_{max} with an increase of ε up to 61 600 M^{-1}cm^{-1}. This small red shift confirms, in agreement with electrochemical data, a limited π-conjugation through the central TCBD segment.

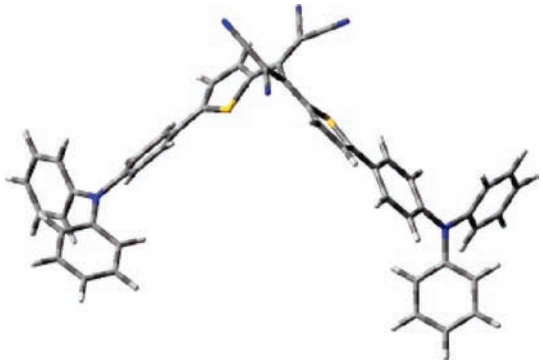

Figure 3. Geometry of **1a** optimized with Gaussian 09 at the B3LYP/6-31G(d,p) level of theory.

The structure of **1a**−**c** has been optimized using DFT with Gaussian 09. In all cases, the geometry shows a significant distortion at the center of the molecule with a dihedral angle of 96.4°, 93.1°, and 94.8°, between the planes containing the two dicyanovinyl groups (Figure 3). This result confirms the restricted π-electron delocalization in the TCBD core in agreement with CV and optical data.

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Such structural feature has been also observed in the solid state for parent compounds.[18a,20,23] As expected, the HOMO is delocalized along the π-conjugated oligothiophene-TPA arms with a prominent contribution of TPA while the LUMO is essentially located on the TCBD core. Thus the HOMO to LUMO electronic transition has a strong ICT character (Figure S25, Supporting Information, for **1a**).

Compounds **1** are thermally stable and TGA curves show a 5% weight loss at 375 °C, 165 and 208 °C respectively for **1a**, **1b** and **1c** (Figure S27–29, Supporting Information, Table 1). The compounds are readily soluble in common organic solvents such as $CHCl_3$, THF or even cyclohexane. The solubility can be related to the non planar structure which may reduce chromophore aggregation.[18a,20]

Thin-films of **1a** have been prepared by thermal evaporation under high vacuum or by spin-casting from $CHCl_3$ solutions. Both kinds of films present the same absorption spectrum with a broadening of the absorption band and a 23 nm red-shift of λ_{max} compared to the solution spectrum (Figure S22, Supporting Information). A band gap E_g of 1.70 eV was estimated from the low-energy absorption onset of the optical spectrum of film of **1a** on glass.

Bilayer heterojunction solar cells have been fabricated by spin-casting films of **1a** on ITO substrates precoated with a 40 nm of PEDOT-PSS, from a 10 mM $CHCl_3$ solution. A 20 nm thick film of C_{60} was then thermally evaporated and the devices were completed by deposition of 100 nm-thick aluminum electrode.

The power conversion efficiency of the various cells has been analyzed under simulated solar illumination in AM 1.5 conditions at 90 mW/cm^2. A cursory analysis of the effect of the thickness of the donor layer showed that best results were obtained with a 25 nm thick layer of **1a** (Table S5, Supporting Information). Average power conversion efficiency (*PCE*) of 1.05% was obtained from analysis of four different cells. The best device gave a short-circuit current density of 3.06 mA cm^{-2} and an open-circuit voltage of 0.97 V. This high voltage can be related to the low HOMO energy level of **1a**. Combined with a fill-factor $FF = 0.33$, these results led to a *PCE* of 1.08% (Figure 4).

Note that bilayer heterojunction solar cells prepared from vacuum deposited films of **1a** of 13 nm thickness, gave an average *PCE* of 0.56% (Table S6, Supporting Information). While these first results are encouraging, the *S* shape of the *J* vs *V* curve suggests that the quality of the interfaces needs to be improved and that better results could be expected for optimized devices.

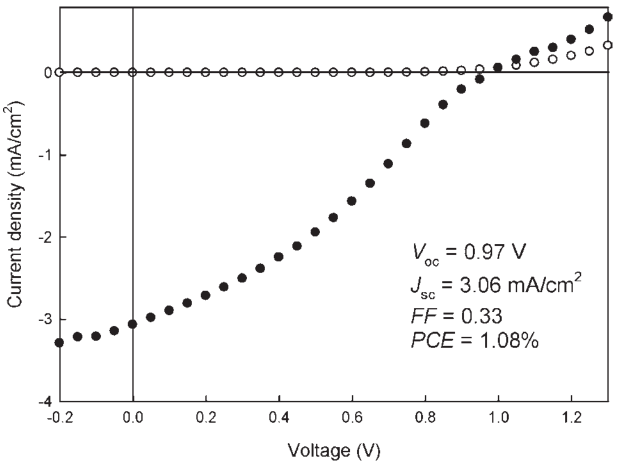

Figure 4. Current vs voltage curves of a bilayer heterojunction **1a**:C_{60}. Open circles: in the dark. Black circles: under AM 1.5 white light illumination at 90 mW/cm^2.

In summary, symmetrical and unsymmetrical D-A-D π-conjugated systems based on a TCBD acceptor have been synthesized. These compounds exhibit strong absorption in the visible spectrum, high oxidation potentials, high stability and good solubility in common organic solvents. Preliminary investigations of their potentialities as donor material carried out on bilayer heterojunction solar cells have given promising results with particularly high cell voltage.

Further investigations of the photovoltaic properties of these materials in bilayer and bulk heterojunction solar cells as well as the synthesis of other members of this class of D-A-D systems are now underway and will be reported in future publications.

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Supporting Information Available. Synthetic procedures and characterization for new compounds, CV and UV–vis data for **8**, geometry optimization for **1** and OSCs characterization. This material is available free of charge via the Internet at http://pubs.acs.org.