

Synthesis of a C₆₀-oligophenylenevinylene hybrid and its incorporation in a photovoltaic device

Jean-François Nierengarten,^{a*} Jean-François Eckert,^a Jean-François Nicoud,^a Lahoussine Ouali,^b Victor Krasnikov^b and Georges Hadziioannou^{*b}

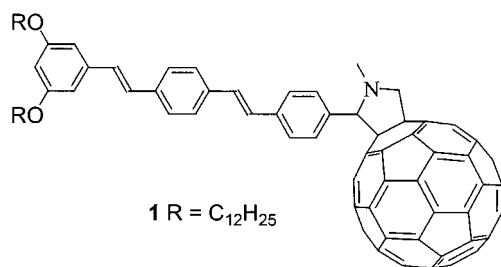
^a Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur and CNRS, 23 rue du Loess, 67037 Strasbourg, France. E-mail: niereng@michelangelo.u-strasbg.fr

^b Department of Polymer Chemistry and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received (in Cambridge, UK) 1st February 1999, Accepted 3rd March 1999

A fulleropyrrolidine derivative bearing an oligophenylenevinylene substituent has been prepared by 1,3-dipolar cycloaddition of an azomethine ylide to C₆₀ and incorporated in a photovoltaic device.

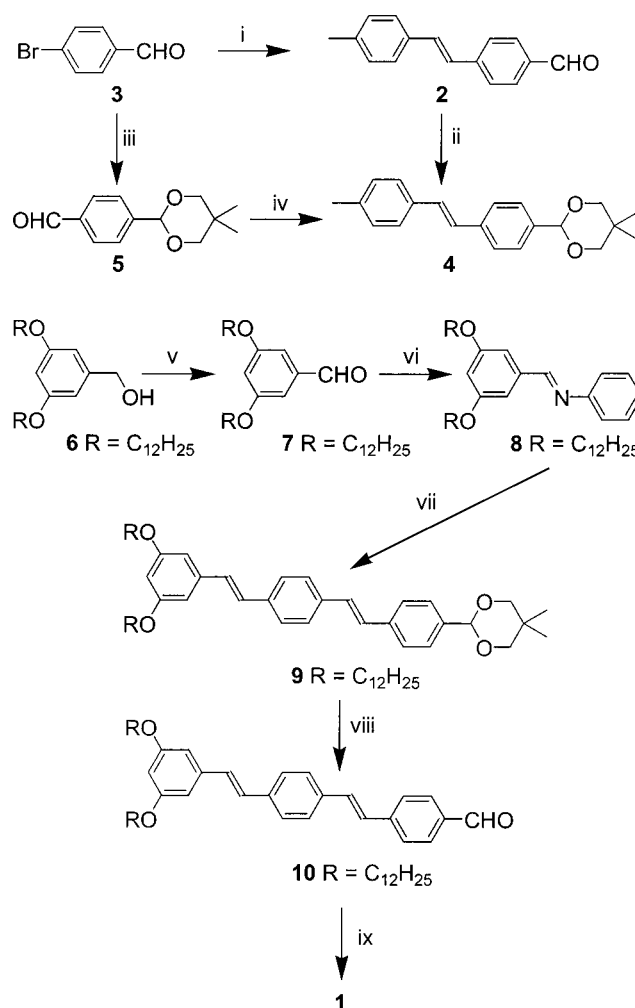
In light of its unusual electrochemical and electronic properties, the fullerene C₆₀ is an attractive functional group for supramolecular assemblies and new advanced materials.¹ For example, photovoltaic devices using thin films of interpenetrating bicontinuous networks of C₆₀ derivative and a number of conjugated polymers such as polyphenylenevinylene or polythiophene have been demonstrated to show promise for large-area photodetectors and solar cells.² In this class of devices the network provides the spatially distributed interfaces necessary for efficient exciton dissociation into electrons and holes, and pathways for their subsequent collection at opposite electrodes. Therefore the film morphology is of crucial importance for the device performance. Usually the donor and acceptor molecules are incompatible and tend to strong and uncontrolled phase separation. An alternative approach to create the bicontinuous network is based on chemically connected donor-acceptor molecules. Recent developments in the functionalisation of fullerenes allows the preparation of covalent C₆₀ derivatives bearing electro- and/or photo-active substituents.³ Some of those systems provide entry into intramolecular processes such as photoinduced charge separation, therefore they appear as potential candidates for the preparation of photovoltaic cells. In this context, we now report the preparation of the fullerene-oligophenylenevinylene hybrid **1** and its utilisation for the construction of a solar energy conversion system.



The synthesis of compound **1** is depicted in Scheme 1. The *E*-stilbene **2** was prepared from 4-methylstyrene and 4-bromobenzaldehyde **3** under Heck conditions with Pd(OAc)₂ as catalyst in toluene–Et₃N in the presence of tri-*o*-tolylphosphine.

Treatment of **2** with 2,2-dimethylpropane-1,3-diol in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) gave **4** in 95% yield. Compound **4** could also be prepared from **3** as follows: protection⁴ (2,2-dimethyl-1,3-propanediol, C₆H₆, *p*-TsOH cat.), subsequent treatment with Bu^tLi in THF followed by quenching with DMF and reaction of the resulting **5** with (4-methylbenzyl)triphenyl-

phosphonium chloride under Wittig conditions. The parent stilbene was thus obtained in 70% yield as an *E*:*Z* isomer mixture in a 55:45 ratio. However, the *Z* isomer could be easily isomerized to the *E* form by treatment with iodine in refluxing toluene. Oxidation of alcohol **6**⁵ with MnO₂ in CH₂Cl₂ followed by condensation of the resulting benzaldehyde **7** with aniline in



Scheme 1 Reagents and conditions: i, 4-methylstyrene, Pd(OAc)₂, tri-*o*-tolylphosphine, Et₃N, toluene, reflux, 48 h, 55%; ii, 2,2-dimethylpropane-1,3-diol, C₆H₆, *p*-TsOH cat., reflux, Dean–Stark trap, 24 h, 95%; iii, 2,2-dimethylpropane-1,3-diol, C₆H₆, *p*-TsOH cat., reflux, Dean–Stark trap, 48 h, then Bu^tLi, THF, –78 °C, 1 h, then DMF, –78 °C to room temp., 1 h, 85%; iv, (4-methylbenzyl)triphenylphosphonium chloride, Bu^tOK, EtOH, room temp., 2 h then I₂, toluene, reflux, 12 h, 70%; v, MnO₂, CH₂Cl₂, 1 h, 89%; vi, aniline, C₆H₆, reflux, Dean–Stark trap, 24 h, 90%; vii, **4**, Bu^tOK, DMF, 80 °C, 2 h, 74%; viii, TFA, CH₂Cl₂, H₂O, room temp., 4 h, 96%; ix, C₆₀, sarcosine, toluene, reflux, 16 h, 43%.

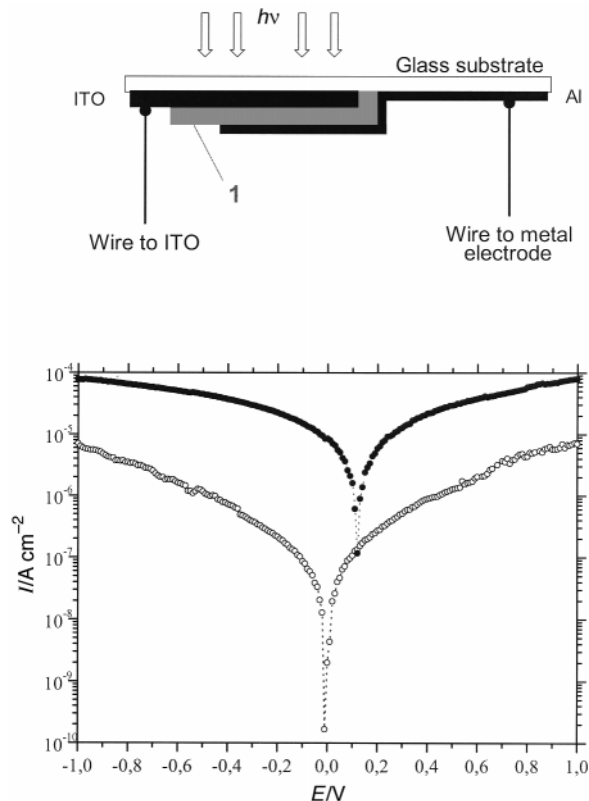


Fig. 1 Top: structure of the photovoltaic cell. Bottom: current–voltage characteristics of the ITO/C₆₀-oligophenylenevinylene/Al device in the dark (○) and under 5 mW cm^{−2} illumination (400 nm) (●).

refluxing benzene afforded **8** in an overall 80% yield. Benzaldimine **8** was subjected to the Siegrist reaction⁶ with stilbene **4** to give protected trimer **9** in 74% yield. Treatment of **9** with CF₃CO₂H in CH₂Cl₂–H₂O (1 : 1) afforded aldehyde **10** in 96% yield. The functionalisation of C₆₀ was based on the 1,3-dipolar cycloaddition⁷ of the azomethine ylide generated *in situ* from **10**. The reaction of C₆₀ with **10** in the presence of an excess of *N*-methylglycine (sarcosine) in refluxing toluene afforded fulleropyrrolidine **1** in 43% yield (or 62% based on the non-recovered C₆₀). All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.[†] The UV–VIS spectrum of **1** corresponds to the sum of the spectra of its two components and shows the characteristic absorptions of a fulleropyrrolidine derivative at 254, 430 and 702 nm as well as the diagnostic oligophenylenevinylene band at 363 nm indicating that there are no significant interactions between the two chromophores in the ground state. Preliminary luminescence measurements show a strong quenching of the oligophenylenevinylene fluorescence in **1**. Charge transfer is expected to occur and compound **1** appears as a potential candidate for the preparation of a photovoltaic cell. The device structure is schematically depicted in Fig. 1. The C₆₀-oligophenylenevinylene films were spin cast, on a glass substrate coated with indium–tin oxide (ITO), from a 4 wt% chloroform solution. The Al electrode was vacuum evaporated on the films to a thickness of 100 nm. Typical current–voltage curves (using ITO as positively and Al as negatively biased electrodes) measured under dark and under light (400 nm, 5 mW cm^{−2}) are presented in Fig. 1. Under the light the device shows clear photovoltaic behaviour with an open-circuit voltage of ca. 0.2 V and a short-circuit current density of 10 μA cm^{−2} corresponding to a collecting efficiency of 1%. Although we do

not know the exact reason of the high dark current under reverse bias, we believe it leads to the relatively low collection efficiency and open-circuit voltage.

We have shown that photovoltaic cells can be prepared with a fullerene–oligophenylenevinylene conjugate. The device efficiency is not yet optimised and further improvements could be expected by utilisation of new fullerene derivatives with a stronger absorption in the visible range.

This work was supported by the CNRS and by a post-doctoral fellowship from The Netherlands Organization for Scientific Research to L. O. We further thank L. Oswald for technical help.

Notes and references

[†] Selected spectroscopic data for **1**: UV–VIS λ_{max}(CH₂Cl₂)/nm 254 (89 800), 363 (63 200), 386 (sh, 38 800), 430 (4700), 702 (340); ¹H NMR (CDCl₃, 400 MHz) δ 0.87 (t, *J* 5.5, 6H), 1.26–1.31 (m, 36H), 1.78 (m, 4H), 2.83 (s, 3H), 3.96 (t, *J* 5, 4H), 4.25 (d, *J* 9.5, 1H), 4.94 (s, 1H), 5.00 (d, *J* 9.5, 1H), 6.38 (t, *J* 1.5, 1H), 6.65 (d, *J* 1.5, 2H), 7.04 (AB, *J* 17, 2H), 7.12 (AB, *J* 17, 2H), 7.48 (s, 4H), 7.61 (d, *J* 8, 2H), 7.82 (br, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.15, 22.71, 26.11, 29.34, 29.44, 29.63, 29.66, 29.69, 31.93, 40.05, 68.10, 69.06, 70.00, 83.35, 101.03, 105.17, 126.85, 126.90, 128.12, 128.54, 128.71, 128.86, 129.68, 135.77, 135.89, 136.43, 136.55, 136.60, 136.71, 136.82, 137.44, 139.15, 139.56, 139.89, 140.14, 141.52, 141.67, 141.84, 141.91, 141.95, 142.02, 142.05, 142.10, 142.15, 142.23, 142.27, 142.54, 142.66, 142.98, 143.13, 144.37, 144.58, 144.69, 145.14, 145.28, 145.52, 145.74, 145.92, 146.05, 146.10, 146.17, 146.27, 146.30, 146.46, 146.71, 147.28, 153.37, 153.98, 156.20, 160.50; FAB–MS: *m/z* 1426.8 (MH⁺). Anal. calc. for C₁₀₉H₇₁O₂N: C 91.76, H 5.02, N 0.98; found: C 91.27, H 5.09, N 1.07%.

- 1 A. Hirsch, *Adv. Mater.*, 1993, **5**, 859; F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317; M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097; L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593; F. Diederich and M. Gomez-Lopez, *Chimia*, 1998, **52**, 551.
- 2 N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474; N. S. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A. J. Heeger, G. Stucky and F. Wudl, *Appl. Phys. Lett.*, 1993, **62**, 585; R. A. J. Janssen, M. P. T. Christiaans, K. Pakbaz, D. Moses, J. C. Hummelen and N. S. Sariciftci, *J. Chem. Phys.*, 1995, **102**, 2628; R. A. J. Janssen, J. C. Hummelen, K. Lee, K. Pakbaz, N. S. Sariciftci, A. J. Heeger and F. Wudl, *J. Chem. Phys.*, 1995, **103**, 788; G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789; B. Kraabel, J. C. Hummelen, D. Vacar, D. Moses, N. S. Sariciftci, A. J. Heeger and F. Wudl, *J. Chem. Phys.*, 1996, **104**, 4267; L. S. Roman, M. R. Andersson, T. Yohannes and O. Inganäs, *Adv. Mater.*, 1997, **9**, 1164.
- 3 S. I. Khan, A. M. Olivier, M. N. Paddon-Row and Y. Rubin, *J. Am. Chem. Soc.*, 1993, **115**, 4919; R. M. Williams, J. M. Zwieter and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 4093; D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft and J.-F. Nierengarten, *Chem. Commun.*, 1996, 2009; H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537; N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten and J.-P. Sauvage, *Chem. Eur. J.*, 1998, **4**, 406; N. Martin, L. Sanchez, B. Illescas and I. Perez, *Chem. Rev.*, 1998, **98**, 2527; F. Effenberger and G. Grube, *Synthesis*, 1998, 1372; S. Llacay, J. Veciana, J. Vidal-Gancedo, J. L. Bourdelande, R. Gonzalez-Moreno and C. Rovira, *J. Org. Chem.*, 1998, **63**, 5201; J. M. Lawson, A. M. Olivier, D. F. Rotherfluh, Y.-Z. An, G. A. Ellis, M. G. Ranasinghe, S. I. Khan, A. G. Franz, P. S. Ganapathi, M. J. Shephard, M. N. Paddon-Row and Y. Rubin, *J. Org. Chem.*, 1996, **61**, 5032; R. M. Williams, M. Koeberg, J. M. Lawson, Y.-Z. An, Y. Rubin, M. N. Padden-Row and J. W. Verhoeven, *J. Org. Chem.*, 1996, **61**, 5055.
- 4 N. Solladié, J.-C. Chambron, C. O. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 906.
- 5 J.-F. Nierengarten and J.-F. Nicoud, *Tetrahedron Lett.*, 1997, **38**, 7737.
- 6 G. Zerban and H. Meier, *Z. Naturforsch. Teil B*, 1993, **48**, 171.
- 7 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519 and references therein.

Communication 9/00829B