

## Synthesis and Photovoltaic Characterization of Fullerene – Oligo(phenylene ethynylene) Hybrids

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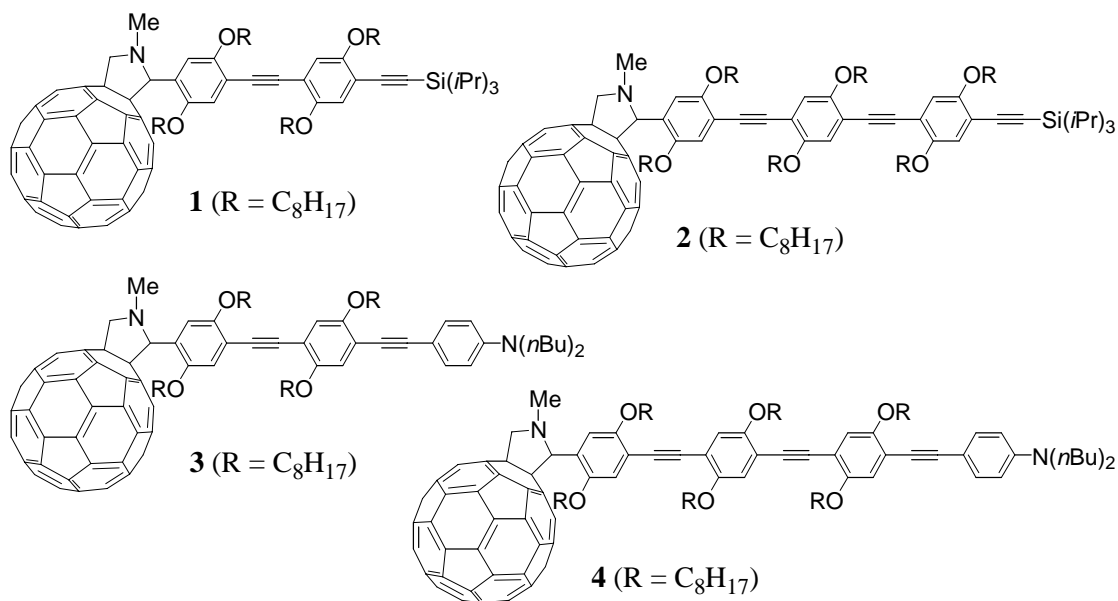
### ABSTRACT

Asymmetrically substituted oligo(phenylene ethynylene) (OPE) derivatives have been prepared by a new iterative method and attached to C<sub>60</sub> molecules by a 1,3-dipolar cycloaddition of the azomethine ylides generated in situ from the corresponding aldehydes and sarcosine. The molecules obtained are suitable for the fabrication of photovoltaic devices based on interpenetrating networks of donors and acceptors, with a characteristic length scale of the network topology smaller than the exciton diffusion length. We have constructed a number of photovoltaic cells incorporating the C<sub>60</sub>-OPEs as the active material between two energetically asymmetric electrode contacts. The device performance has been examined and the functional characteristics have been determined too. These seem to depend systematically on the nature of the attached end-group and on the length of the donating moiety.

### INTRODUCTION

Organic semiconducting materials are being extensively studied in the field of photovoltaics aiming to the broad production of plastic solar cells. Appropriately modified C<sub>60</sub> derivatives chemically linked with  $\pi$ -conjugated polymers are currently considered to be the most promising candidates for such applications following the discovery of ultrafast, photoinduced charge transfer between them [1-5]. As a part of this research, we have recently shown that fullerene derivatives in which an oligophenylenevinylene (OPV) group is attached to C<sub>60</sub> can be incorporated into photovoltaic cells [4]. The large interfacial area between donor and acceptor phases, which are formed spontaneously during spin coating, supports the efficient charge separation in these mixtures. This molecular approach for solar energy conversion appears to be particularly attractive since the formation of a bicontinuous network prevents any problems arising from bad contacts at the junction, as observed for polymer/C<sub>60</sub> blends. Furthermore, this new synthetic approach also offers great versatility for design tuning the photovoltaic system.

In the present study we report the preparation of such organic solar cells obtained from the fullerene-oligophenyleneethynylene (OPE) derivatives 1-4. For compounds 1 and 2, the efficiency of the resulting photovoltaic devices is similar to those prepared from corresponding fullerene-OPV conjugates [4-5]. Interestingly, by increasing the donating ability of the



**Figure 1.** The compounds 1-4 presented in this work.

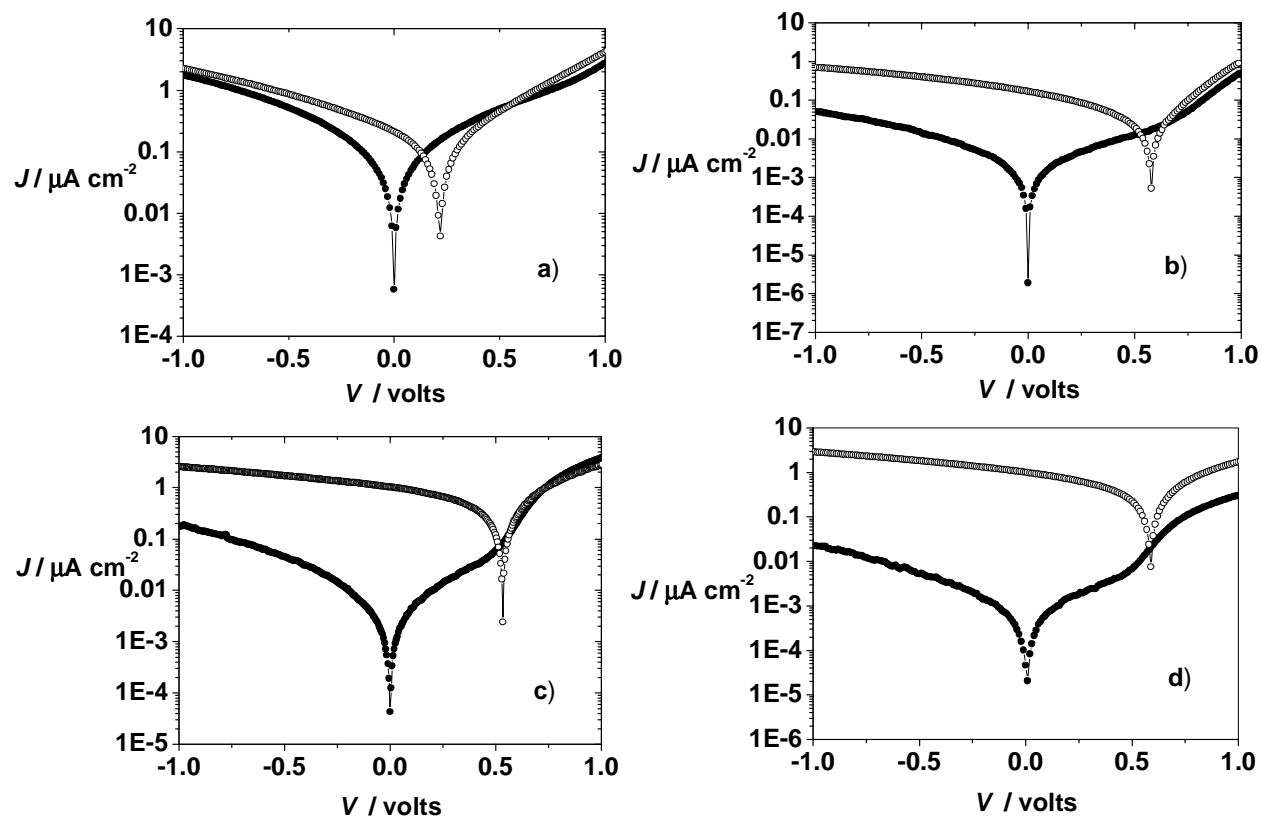
conjugated oligomer substituents in 3 and 4 due to the presence of the aniline group, the efficiency and the sensitivity of the photovoltaic devices are increased by one order of magnitude. The latter observation shows clearly the advantage of our molecular approach allowing structure/activity relationships.

## EXPERIMENTAL DETAILS

The preparation of compounds 1 and 2 has been recently reported [6]. The synthesis of 3 and 4 is depicted in figure 2. Treatment of the protected terminal alkynes 5 and 6 with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) at 0°C afforded 7 and 8 in 91 and 92% yields, respectively [6]. Subsequent Pd-catalyzed cross-coupling reaction with 4-iodo-*N,N*-dibutylaniline then gave 9 and 10 [7]. The functionalization of  $C_{60}$  was based on the 1,3-dipolar cycloaddition of the azomethine ylide generated in situ from aldehydes 9 and 10 [8]. The reaction of  $C_{60}$  with 9 in the presence of an excess of *N*-methylglycine (sarcosine) in refluxing toluene afforded fulleropyrrolidine 3 in 39% yield. Compound 4 was obtained in 45% yield under similar conditions from 10,  $C_{60}$  and sarcosine. For all the  $C_{60}$ -OPE derivatives 1-4, the UV/Visible spectrum corresponds to the sum of the spectra of their two components indicating no significant ground state interactions between the two chromophores. Preliminary luminescence measurements have shown a strong quenching of the OPE fluorescence by the fullerene moiety in 1-4 indicating the occurrence of intramolecular photo-induced processes.

Compounds 1-4 have been tested as active materials in photovoltaic cells. The substrates utilized were always 20 mm × 20 mm glass slides coated with indium tin oxide (ITO). Just





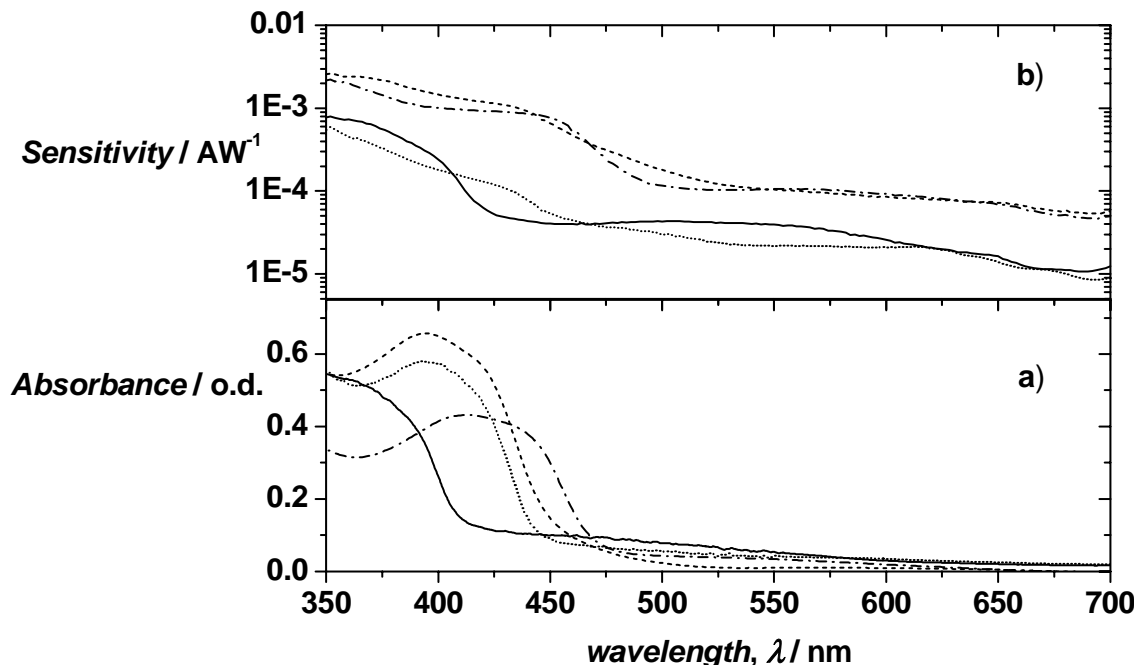
**Figure 3.** J/V characteristics in the dark (-●-) and under illumination (-○-) for a) ITO/PEDOT-PSS/1/Al; b) ITO/PEDOT-PSS/2/Al; c) ITO/PEDOT-PSS/3/Al; d) ITO/PEDOT-PSS/4/Al.

## DISCUSSION

In the dark, the current in reverse bias is higher by two orders of magnitude for the ITO/PEDOT-PSS/1/Al and ITO/PEDOT-PSS/3/Al devices when compared to the devices prepared from the corresponding higher homologues 2 and 4. It is likely that the derivatives with the shortest OPE moieties exhibit better charge transport properties as their intrinsic fullerene/OPE weight ratio is higher. The optimized fullerene/polymer weight ratio used in the

**Table I.** The performance characteristics measured for all the photovoltaic devices prepared utilizing compounds numbered 1-4.

Compound	$V_{OC} / V$	$J_{SC} / A cm^{-2}$	FF	T %	$S_{400} / A W^{-1}$	$\eta_{e,400} \%$
1	0.22	2.05E-7	0.27	55	2.41E-4	1.2E-3
2	0.58	2.04E-7	0.22	27	1.81E-4	2.6E-3
3	0.54	1.16E-6	0.32	22	1.46E-3	2.0E-2
4	0.59	1.06E-6	0.29	39	1.01E-3	1.8E-2



**Figure 4.** Plots of absorbance (a) and sensitivity (b) as a function of the wavelength for all the devices (ITO/PEDOT-PSS/1/Al: — ; ITO/PEDOT-PSS/2/Al: ••• ; ITO/PEDOT-PSS/3/Al: - - - ; ITO/PEDOT-PSS/4/Al: - • -).

most efficient polymer solar cells is 4 [1b]. For compounds 1-4, the fullerene/OPE weight ratio is smaller than 1, this presumably lowers both the power conversion efficiency and the open-circuit voltage of the resulting solar cells.

Under the light, all the devices show clear photovoltaic behavior. Interestingly, the performances of the devices prepared from the *N,N*-dialkylaniline terminated derivatives 3 and 4 are significantly improved when compared to those obtained with 1 and 2. This can be related to the differences seen in their first oxidation potentials determined by cyclic voltammetry measurements [9]. Effectively, due to the increased donating ability of the OPE moiety in 3 and 4 when compared to 1 and 2, the energy level of their charge separated states resulting from a photoinduced electron transfer (PET) is significantly lower in energy. Therefore, the thermodynamic driving force is more favorable, thus PET which is one of the key step for the photocurrent production must be more efficient for 3 and 4 [5]. As a result, the power conversion efficiency and the sensitivity of the respective devices over the whole spectral range (figure 4) are increased by one order of magnitude.

## CONCLUSIONS

We have shown that the fine-tuning of a unique molecule in a photovoltaic cell allows to easily obtain structure/performance relationships for a better understanding of the system examined. In particular, we have shown that the efficiency of the devices can be significantly

improved by increasing the donating ability of the OPE moiety and the charge transport properties can be modulated by the intrinsic fullerene/OPE weight ratio. Further improvements could be expected by the utilization of related fullerene derivatives with a stronger absorption in the visible range and a higher fullerene/OPE weight ratio.

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