

Design, synthesis and photovoltaic properties of [60]fullerene based molecular materials

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Abstract

The possibility to use new organic semiconductor materials, in place of silicon wafers, in the fabrication of photovoltaic devices on substrates offer the prospect of lower manufacturing costs, particularly for large area applications. Thus, one of the most promising areas in fullerene research involves its potential application, mixed with conjugated polymers, in mimicking photosynthesis and in the related solar energy conversion. The tendency to phase segregation in blends of C₆₀ derivatives and conjugated polymers has to be optimized to improve both charge photogeneration and transport in photovoltaic devices. In order to optimize device performances, a great deal of work has been devoted to the development of new device architectures and to elucidating the photophysical processes underlying the photovoltaic response. However, optimization of cells has been carried out with just a few materials and recent findings show that new developments can be very successful if a broader scope of materials in the composite layers becomes accessible. Thus, in this communication we present new approaches toward the synthesis of [60]fullerene derivatives specifically designed to be used in the fabrication of photovoltaic devices. (i) the first approach involves the synthesis of functionalized C₆₀ and C₇₀ derivatives with enhanced solubility; (ii) the second approach is directed to the synthesis of systems containing a conjugated moiety antenna covalently linked to the C₆₀ unit. Together with the synthesis of these new materials, electrochemical and photophysical investigations have been also carried out. Photovoltaic devices have been fabricated with selected materials.

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1. Introduction

The most recent and efficient polymer solar cells fabricated today are based on the concept of bulk heterojunction. They consist of a p-type conjugated polymer with an acceptor moiety mixed into it as an n-type material. The different solubilities of the two components in the organic

solvents used for the film preparation and their limited miscibility cause phase segregation. This tendency to phase segregation has to be tailored to optimize both charge photogeneration and transport. Since the charges are preferentially formed at the donor–acceptor interface an intimate mixing of the donor and acceptor is beneficial for charge generation. On the other side it is necessary to attain an efficient transport to the electrodes of holes through the donor and of electrons through the acceptor phase. For these reasons the donor and acceptor components have to be organized towards nanoscopic phase segregated bicontin-

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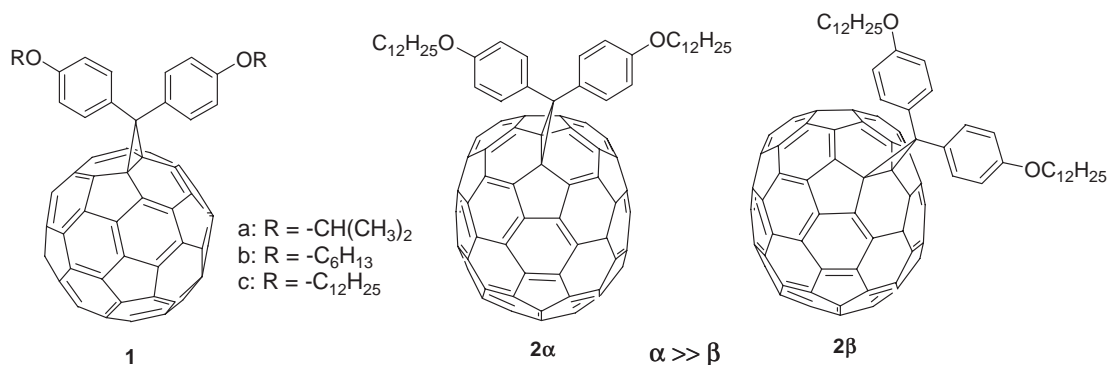


Fig. 1.

uous network. Indeed the most significant improvements of the device efficiencies have been attributed to more favorable morphologies [1]. We present here two approaches in order to tailor the phase separation in organic films: the first approach involves the synthesis of functionalized C_{60} derivatives with enhanced solubility and the second strategy is directed to the synthesis of systems containing a conjugated moiety antenna covalently linked to the C_{60} unit.

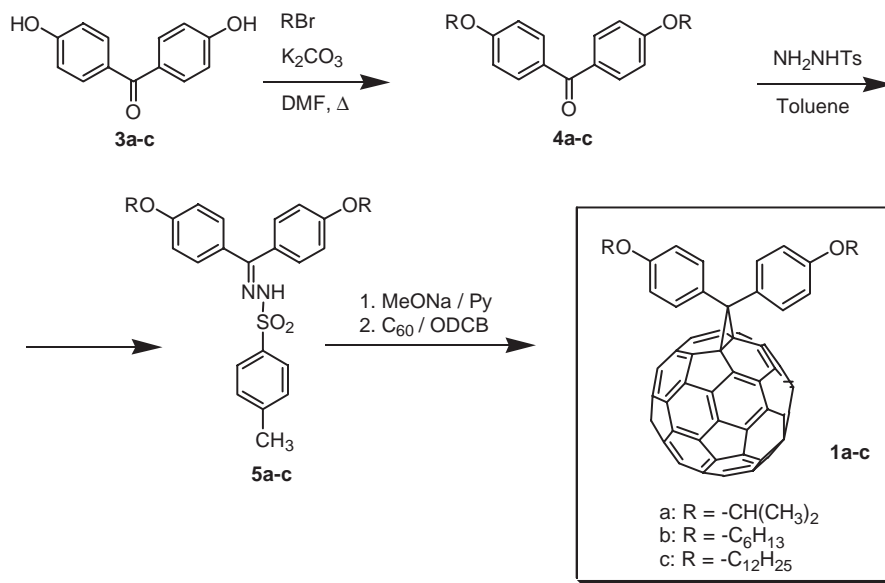
1.1. Synthesis of fullerene derivatives with enhanced solubility

As stated above, best efficiencies in photovoltaic devices have been attributed to more favorable morphologies. Thus, we present here the synthesis of a series of fullerene derivatives (**1**, **2 α** , **2 β** , Fig. 1) exhibiting enhanced solubility.

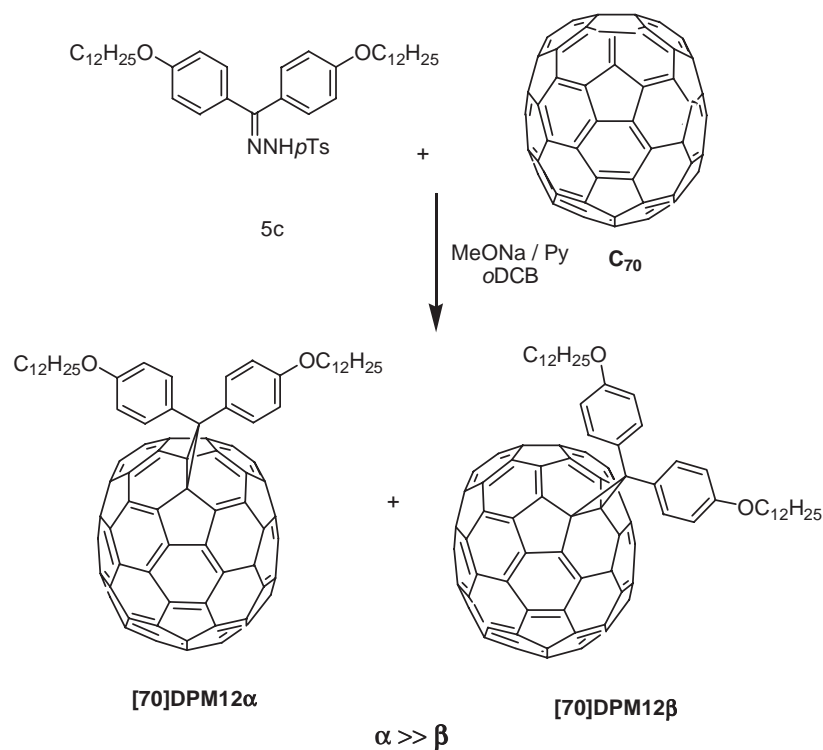
Compounds **1** are diphenylmethanofullerene (DPM) derivatives endowed with two alkoxy chains. Reaction of 4,4'-dihydroxybenzophenone (**3**) with the corresponding alkyl bromide in dry dimethylformamide in the presence of

potassium carbonate allows to obtain the corresponding dialkoxy-substituted benzophenones (**4a–c**). Further reaction of **4a–c** with tosylhydrazine in toluene using *p*-toluenesulfonic acid as catalyst afforded the corresponding tosylhydrazones **5a–c**. Subsequent 1,3-dipolar cycloaddition reaction of the diazo compound generated in situ upon heating an *o*-dichlorobenzene solution containing *p*-tosylhydrazones and [60]fullerene in the presence of sodium methoxide allowed to obtain the corresponding ethanofullerenes [60]DPM-3, [60]DPM-6 and [60]DPM-12 (**1a–c**) (Scheme 1).

Similar 1,3-dipolar cycloaddition to C_{70} leads, after purification, to a mixture of regioisomers which could not be separated by flash chromatography (Scheme 2). In contrast to the highly symmetric [60]fullerene, [70]fullerene possesses five sets of inequivalent carbon atoms [2] presenting a variety of bonds with different reactivity. The most strained, and therefore more reactive, [70]fullerene bonds are found at the poles (type α , surrounded by type β) whereas the flatter equatorial region contains a number of different, less curved bonds [3]. Thus, from all the possible



Scheme 1.



Scheme 2.

monoadducts that can be formed, we only observed the formation of two monoadducts which were assigned to those corresponding to the more strained bonds in a proportion of **[70]DPM-12 α : [70]DPM-12 β** 10:1 according to the $^1\text{H-NMR}$ spectrum. Due to its C_s symmetry, in the $^{13}\text{C-NMR}$ spectrum of **[70]DPM-12** can be clearly appreciated between 155.6 and 130.6 ppm the 34 sp 2 signals corresponding to the fullerene moiety together with the four signals corresponding to the benzene residues. At 69.9 and 72.0 ppm can be seen the signals corresponding to the sp 3 carbons of the cyclopropane ring and, the signal around 40 ppm, is assigned to the sp 3 bridgehead carbon. The greater number of signals which appear with a remarkably lower intensity most likely correspond to the less symmetric “ β -type” addend.

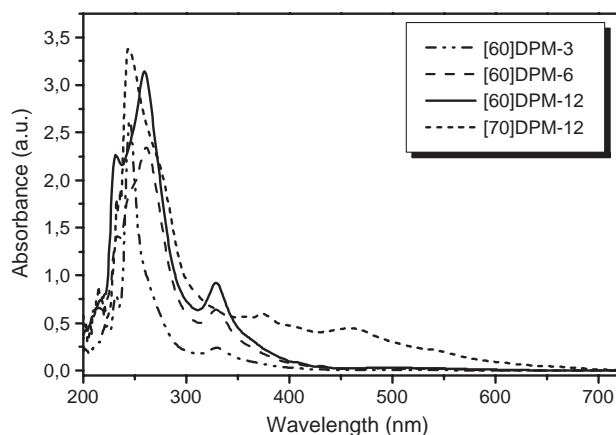


Fig. 2. UV–Vis spectra of DPM series in dichloromethane.

The characteristic bands of the C_{70} moiety at 579 and 532 cm^{-1} can be appreciated in the IR spectrum of the sample.

The UV–Vis spectra of the **[70]DPM-12** mixture together with that of the three different **[60]DPM** in dichloromethane solutions are depicted in Fig. 2.

As it was previously reported for the PCBM series, [4] and also when comparing unsubstituted C_{60} and C_{70} , [5] in the DPM series, a significant higher absorption coefficient in the visible region is observed when comparing **[70]DPM-12** with the other **[60]DPM**.

Concerning the electrochemical properties of these materials, they all exhibit four quasireversible reduction waves corresponding to the first four reduction steps of the fullerene core. The observed values – see Table 1 – are cathodically shifted in comparison with pristine C_{60} due to the saturation of a double bond of the C_{60} unit [6].

It is worth mentioning that **[70]DPM12** shows a similar acceptor ability to that of the **[60]DPM** analogues. This fact

Table 1
Redox potentials (in Volts)^a measured in dichloromethane solutions

Comp.	E^1 cp	E^2 cp	E^3 cp	E^4 cp
C_{60}	–0.59	–1.01	–1.47	–1.94
C_{70}	–0.58	–0.99	–1.41	–1.81
[60]DPM3	–0.67	–1.06	–1.59	–2.04
[60]DPM6	–0.70	–1.05	–1.59	–2.02
[60]DPM12	–0.70	–1.11	–1.63	–2.08
[70]DPM12	–0.67	–1.06	–1.47	–1.88

^a V vs. SCE; working electrode: GCE; reference electrode: Calomel; counter electrode: Pt; 0.1 M Bu_4NClO_4 ; oDCB/MeCN (4/1); Scan rate: 200 mV/s.

is in agreement with that observed in pristine C₆₀ and C₇₀ which show an almost identical redox behavior [7].

We have fabricated photovoltaic devices with mixed DPM:poly(2-methoxy-5-[3',7'-dimethyloctyloxy]-*p*-phenylene vinylene (MDMO-PPV) (4:1 w/w) films [8].

The performance characteristics of the photovoltaic devices are collected in Table 2 and the I–V curves are depicted in Fig. 3.

The efficiencies of these devices are low in comparison with similar devices fabricated with mixtures of PCBM and MDMO-PPV [1,4]. However, it is worth mentioning that, in this case, devices have not been optimised. Devices were built according to parameters found to be optimum with PCBM samples and it should be taken into account that since the first reports in photovoltaic devices using PCBM almost one decade ago, [9] different parameters (electrodes, device configuration, semiconducting polymers, solvent, . . .) have been modified thus allowing an improvement in device performances [1,10]. In fact, simply changing the solvent used from toluene to chlorobenzene in the case of MDMO-PPV and PCBM resulted in a three-fold increased AM1.5 spectrum power conversion efficiency up to 2.5% [1].

1.2. Synthesis of dyads based on conjugated systems covalently attached to fullerene C₆₀

The second approach in order to obtain uniform and high quality thin films for device fabrication involves the preparation of dyads containing conjugated oligomers and dendrimers covalently linked to the C₆₀ core.

During the last years, oligomers has helped to bridge the gap between the chemistry of low molecular weight compounds and those of polymeric materials [11,12]. Importantly, the study of monodisperse, well-characterized conjugated oligomers facilitated the establishment of structure–activity relationships with the overall objective being to rationalize the properties of the parent polydisperse polymers.

In recognition of this importance, we present here several donor–acceptor arrays which have been probed in time-resolved and steady-state photolytic experiments. One of the most striking features of these systems is that their excited-state dynamics are dominated by a competition between rapid energy and electron-transfer reactions. The outcome of this contest depends largely on the nature of the

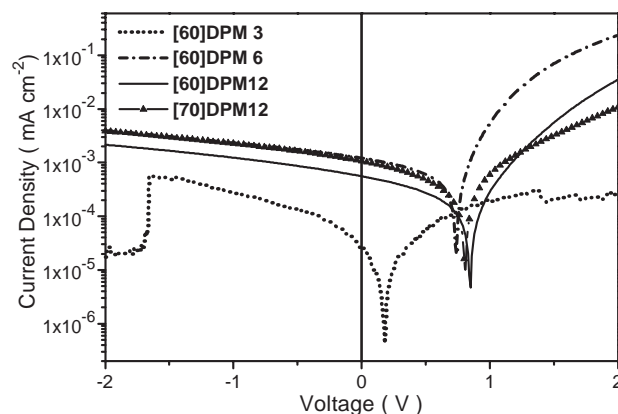


Fig. 3. I/V characteristic for DPM derivatives. All the samples were spin-coated mixed with MDMO-PPV in a 4:1 ratio (w/w) in oDCB.

π -conjugated system, as well as on the number of repeating units in the oligomer and the nature of the peripheral units in the dendrimer.

Among the suitable protocols for the functionalization of fullerenes, the 1,3-dipolar cycloaddition of azomethine ylides to C₆₀ has emerged as an important methodology for the production of stable fullerene derivatives [13]. To date, a broad spectrum of intriguing fulleropyrrolidine derivatives, bearing various electro and/or photoactive addends, have been synthesized via this procedure [14]. Therefore, we targeted at the synthesis of conjugated systems with one aldehyde group, enabling us to adapt this synthetic methodology for the production of C₆₀-based dyads.

1.2.1. Conjugated oligomer–C₆₀ fullerene dyads

In Scheme 3 are shown the new C₆₀-conjugated oligomer dyads (**6a–d**) obtained through 1,3-dipolar cycloaddition of oligomers endowed with an aldehyde functionality [15] to C₆₀ in the presence of sarcosine in refluxing toluene. Due to the presence of the long alkoxy substituents, these dyads are highly soluble in common organic solvents, and complete spectroscopic and electrochemical characterization was achieved.

The electrochemical features of these dyads were probed by cyclic voltammetry at room temperature. As a general feature, dyads **6a–d** give rise to three quasireversible one-electron reduction waves that reflect the first three one-electron reduction steps of the fullerene cores. A closer inspection of the data reveals that the first reduction potential values of these dyads are all similar and compare quite well with that of an unsubstituted fulleropyrrolidine reference. As we discussed above, these reduction potential values are shifted to more negative values relative to that of pristine [60]-fullerene due to the saturation of a double bond of the C₆₀ core, which, accordingly, raises the lowest unoccupied molecular orbital (LUMO) energy of the resulting fullerene derivative. On the other hand, the redox behavior of the conjugated π -systems shows an increase of the donor strength, when going from dihexyloxynaphthalene (**6a**): Eox

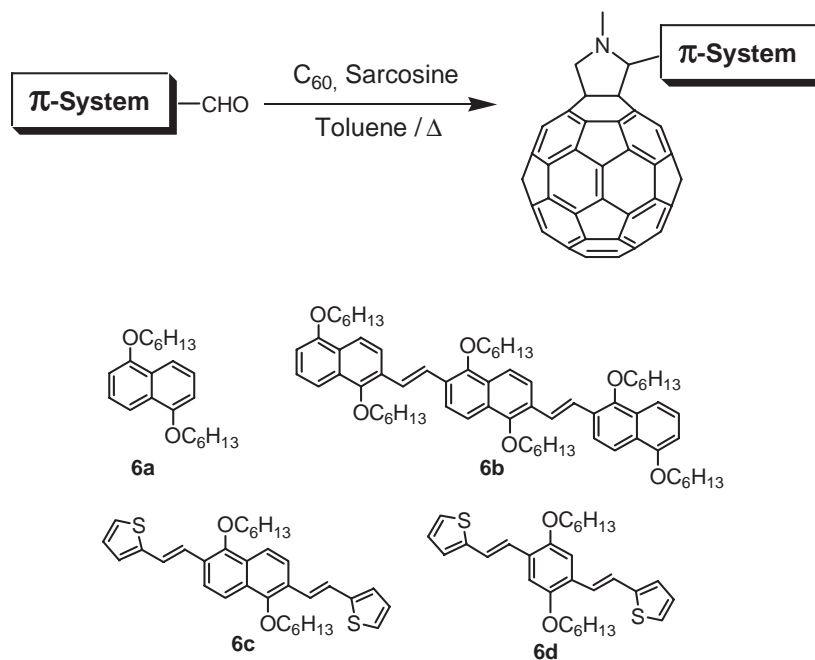
Table 2

Performance characteristics of the photovoltaic devices

Comp.	J_{sc}^a	V_{oc}^b	FF	$\eta_{AM\ 1.5}$ [%]
[60]DPM3	0.03	0.18	0.201	
[60]DPM6	1.21	0.74	0.34	0.38
[60]DPM12	0.56	0.85	0.35	0.21
[70]DPM12	1.1	0.81	0.285	0.3

^a in mA/cm².

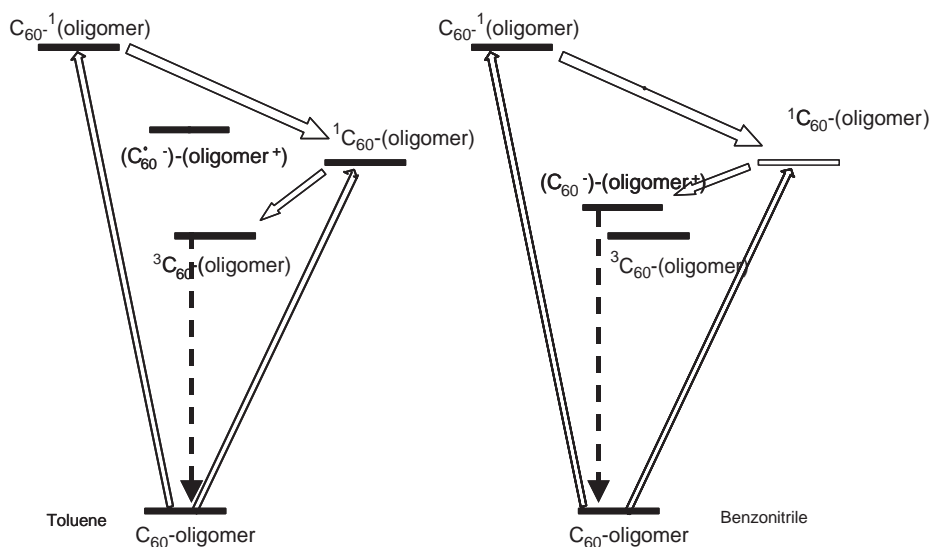
^b In Volts.



: 1.41 V) to the trimeric analogue (**6b**: Eox : 1.31 V), and also upon replacing the peripheral naphthalene units in the trimer by the π -excedent thiophene ring (**6c**: Eox : 1.20 V). The best results, in terms of oxidation, were observed for the p-conjugated system, in which the central naphthalene moiety is replaced by a phenylene unit (**6d**: Eox : 1.01V).

Photophysical investigations performed for dyads **6a–d** show that by controlling the structure of fluorescent π -conjugated systems, the outcome of an ultra rapid intramolecular deactivation of a photoexcited oligomer core was successfully shifted from an all energy transfer to an all electron-transfer scenario.

In particular, the different oxidation potentials of, for example, dihexyloxynaphthalene (i.e., monomeric and trimeric form), dihexyloxybenzene/thiophene and dihexyloxynaphthalene/thiophene moieties helped to direct the competition between these two transfer channels. Hereby, the relative position of the charge-separated state in reference to the fullerene singlet excited state determines the nature of the photoproduct: only the energetically lowest lying state is populated in high yields. In Fig. 4 are shown the photophysical processes observed for dyad **6d** in toluene (left) and benzonitrile (right) solutions acetonitrile. The stabilization of the charge separated state in the more polar



benzonitrile solution favours the electron transfer process while an energy transfer process is favoured in the less polar toluene solutions.

Photovoltaic devices [16] confirm the efficient photo-induced charge generation within one of the investigated donor–acceptor ensembles (**6d**). Spectrally resolved photocurrent measurements revealed contributions from both the oligomer and the fullerene moiety to the photocurrent generation.

Moreover, photovoltaic devices showed white light efficiencies up to 0.2%. This is one of the highest values ever reported for a solution processed single component organic solar cell. In fact, charge generation, as well as electrical current rectification, may indeed be cooperatively realized within this molecular donor–acceptor ensemble, thereby combining both essential features for photovoltaics within a single molecule.

1.2.2. Conjugated dendron– C_{60} fullerene dyads

We have also investigated new D-B-A systems in which two (**7a**) or four (**8a**) dibutylaniline or dodecyloxynaphthalene (**7b**, **8b**) electron donors are located at the peripheral positions of well-defined phenylenevinylene-based dendrons and a fullerene acceptor at the focal point of the dendrimer (Fig. 5).

The synthetic procedure for the preparation of these dendron– C_{60} dyads is based also on the 1,3-dipolar cycloaddition reaction of C_{60} with aldehyde functionalized dendrons [17]. The presence of long alkyl chains at peripheral positions of the dyads provided good solubility

of these compounds which have allowed full spectroscopic and electrochemical characterization of these new materials.

The UV–vis spectra of dyads **7a,b** and **8a,b** in dichloromethane solutions are a superposition of the spectra of the individual chromophores (i.e., C_{60} and the conjugated dendron) thus indicating lack of interaction between the electroactive moieties in the ground state.

The electrochemical features of dyads **7a,b** and **8a,b** were probed by cyclic voltammetry at room temperature. A toluene–acetonitrile solvent mixture (4:1 v/v) and tetra-n-butylammonium perchlorate (0.3 mg/ml) as supporting electrolyte were used in a conventional three-compartment cell, equipped with a glassy carbon, SCE and platinum wire as working electrode, reference electrode and auxiliary electrode, respectively. As a general feature, dyads (**7a,b** and **8a,b**) give rise to three quasireversible one-electron reduction waves that reflect the first three one-electron reduction steps of the fullerene cores. As for the oligomer-based dyads, reduction potential values are shifted to more negative values relative to pristine C_{60} due to the saturation of a double bond of the fullerene core. A closer inspection of the data reveals that the first reduction potential values of these dyads are all very similar and compare quite well with that of the unsubstituted fulleropyrrolidine reference in which the same double bond of the fullerene core is saturated.

The redox behavior of the stilbenoid dendrons show an increase of the donor strength when going from the dodecyloxynaphthalene-based (Eox~1.30 V vs. SCE) to the dibutylaniline-based systems (Eox~0.7 V vs. SCE).

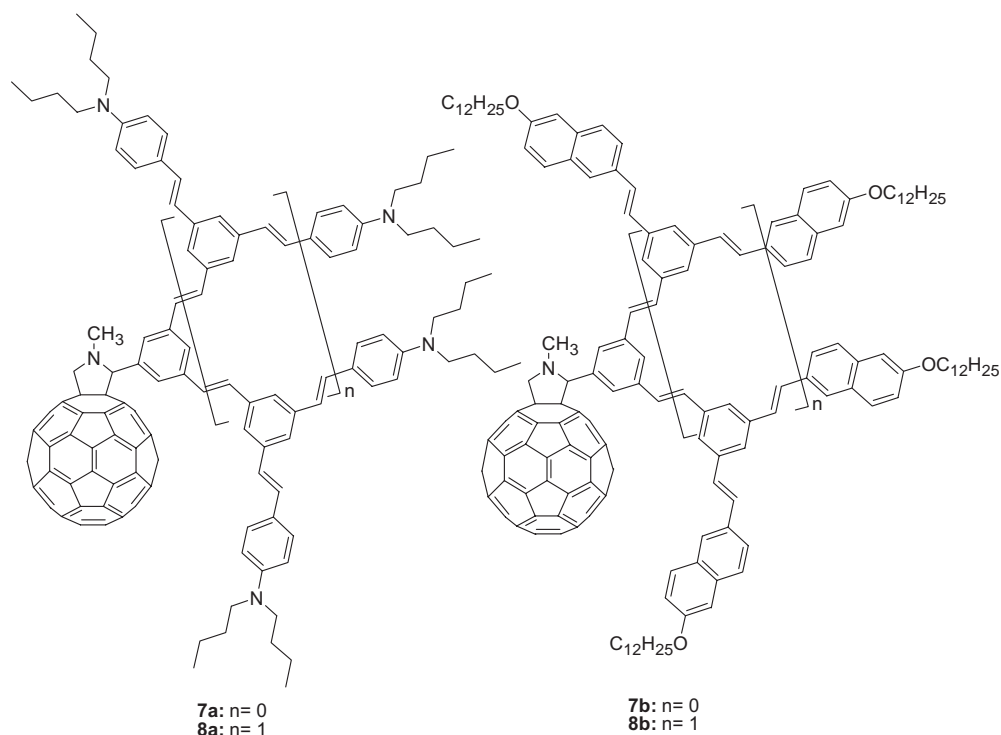


Fig. 5.

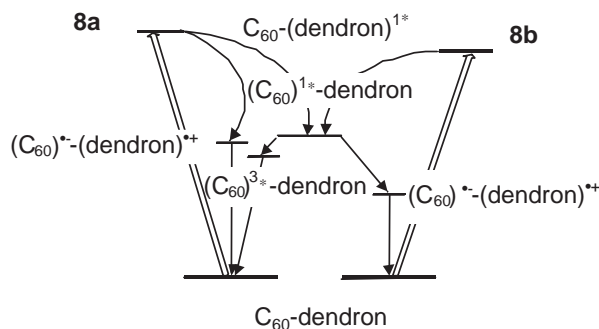


Fig. 6. Photophysical processes observed after photoexcitation of dyads **8a** (left) and **8b** (right).

This fact is in agreement with the better donor ability of the dibutylaniline group in comparison with that of dodecyloxynaphthalene.

Photophysical investigations show that, in all dyads, an efficient and rapid energy transfer, as confirmed in a series of steady-state and time-resolved photolytic experiments, dominates the deactivation of the initially excited dendron antennas, generating the fullerene singlet excited state in nearly quantitative yields. A detailed spectroscopic and kinetic analysis prompts, nonetheless, to an alternative intramolecular electron transfer, from which an energetic $C_{60}\bullet^-(\text{dendron})\bullet^+$ radical pair evolves. Most importantly, variation of the energy gap modulates the character of this electron transfer reaction: Depending on the energetic position of the $C_{60}\bullet^-(\text{dendron})\bullet^+$ radical pair either a competitive (i.e., **7b**, **8b**) or a sequential pathway (i.e., **7a**, **8a**) is activated (Fig. 6).

A final comment should address the comparison between C_{60} -dendron dyads and the previously presented C_{60} -oligomer systems. First, the meta-linkage of the stilbene unit in the dendron breaks the π -conjugation. This allows the control over the effective conjugation length. Second, the rigid dendrons function as efficient mediators for the electron coupling between electron donor and electron acceptor. As a consequence, highly stabilized and spatially well-separated charge separated species are generated which give rise to a profound distance behavior.

Work is now in progress in order to check the behavior of these dendron-based dyads in photovoltaic devices.

2. Summary

In summary, we have developed new strategies toward the synthesis of C_{60} derivatives for photovoltaic applications. A first strategy involves the synthesis of highly soluble fullerene derivatives. Preliminary investigation in the fabrication of solar cells with blends of **DPM** derivatives and PPV show an increase in the open circuit potential of around 100 mV in comparison with the extensively used PCBM system in identical cell configurations. Thus a V_{oc} higher than 800 mV were obtained for **[60]DPM12** and

[70]DPM12 and they were reproducible for almost all devices prepared. Thus, this material seems to be a suitable candidate to be investigated in depth in optimized solar cells.

The second strategy involves the synthesis of dyads containing conjugated oligomers and dendrimers covalently linked to the C_{60} core. A remarkable control on the energy and electron transduction can be achieved through chemical engineering of the corresponding oligomer and dendrimer. Photovoltaic devices using dyad **6d** as active layer showed white light efficiencies up to 0.2% being this is one of the highest values ever reported for a solution processed single component organic solar cell.

These findings suggest that these novel systems are of interest for further investigations toward the fabrication of optimized organic solar cells.

Acknowledgements

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