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# Synthesis and electronic properties of donor-linked fullerenes towards photochemical molecular devices

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## Abstract

We report our recent progress in the synthesis and the study of donor-linked fullerenes. The synthesis of C<sub>60</sub> polyadducts with well defined three-dimensional structure provides versatile building blocks for the preparation of porphyrin–fullerene derivatives with unusual stereochemical and electronic properties. Phenanthroline ligands substituted with fullerene-functionalized dendritic wedges and their copper(I) complexes have been prepared. Electrochemical and photophysical investigations have shown that the bis(phenanthroline)copper(I) central core is somehow buried in a dendritic black box. Finally, fullerene–oligophenylenevinylene hybrids have been synthesised in order to provide a molecular approach to photovoltaic conversion, and to prevent the morphology problems resulting from the phase separation in donor–acceptor composites. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. Fullerene; C. Spectrophotometry; D. Electronic properties, Electrochemical properties, Optical properties

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## 1. Introduction

In light of their unusual physical and chemical properties, fullerenes and their derivatives appear to be attractive candidates for the construction of supramolecular assemblies and advanced materials [1–3]. The recent progress in the chemistry of C<sub>60</sub> [4] allows the preparation of many fullerene derivatives covalently bound to donor moieties [5,6]. These systems provide entry into intramolecular processes such as energy and electron transfer

[5–44]. It should be pointed out that the C<sub>60</sub> group appears to be a particularly interesting electron acceptor in photochemical molecular devices because of its symmetrical shape, its large size and the properties of its  $\pi$ -electron system. The characteristics of C<sub>60</sub> are in stark contrast with those of common acceptors with smaller size such as benzoquinone. Actually, accelerated charge separation and decelerated charge recombination has been observed in a fullerene-based acceptor–donor system when compared to the equivalent benzoquinone-based system [26]. This has been interpreted simply by the smaller reorganization energy ( $\lambda$ ) of C<sub>60</sub> compared with those of small acceptors: the smaller reorganization energy of C<sub>60</sub> positions the photoinduced charge separation rate upward along the normal region of the Marcus parabolic curve, while forcing

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the charge recombination rate downward in the inverted region. The efficient photogeneration of long lived charge-separated states by photoinduced electron transfer is of particular interest for initiating photocatalytic reactions (artificial photosynthesis) or for solar energy conversion (photovoltaic cells). Here, we report our recent progress in the synthesis and the studies of donor-linked fullerenes. We also show that such compounds can be used for a molecular approach to photovoltaic cells. In this case, the fullerene-donor derivative is not only able to generate electrons and holes under light irradiation, but it also provides pathways for their subsequent collection at opposite electrodes, and a photocurrent is obtained.

## 2. Fullerene-substituted porphyrins

Since the first reported preparation of a C<sub>60</sub>-linked porphyrin by Gust et al. [23], several other fullerene-porphyrin hybrids have been described [24–44] and intramolecular processes such as electron and energy transfer have been observed in some of these compounds [23–44]. All the reported porphyrin–C<sub>60</sub> dyads have been usually synthesized by reaction of a preconstructed porphyrin derivative with C<sub>60</sub> itself or a C<sub>60</sub>-acid derivative [23–44]. We report herein the preparation and the electrochemical properties of the soluble porphyrins **1** and **2** substituted with two and four fullerene subunits, respectively. Compounds **1** and **2** were prepared by reaction of C<sub>60</sub>-benzaldehyde **3** with dipyrrol-2-yl methane **4** [45] and pyrrole, respectively, in the presence of an acid catalyst (Fig. 1). The C<sub>60</sub>-benzaldehyde **3** was synthesized as depicted in Fig. 2.

*N,N'*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of diol **5** with the malonic mono-ester **6** [46] yielded bismalonate **7**. The functionalization of C<sub>60</sub> was based on the highly regioselective Diederich reaction [47–49] which yielded macrocyclic bisadducts of C<sub>60</sub> resulting from a macrocyclization reaction of the carbon sphere with bismalonate derivatives in a double Bingel addition [50]. Treatment of C<sub>60</sub> with **7**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the C<sub>s</sub>-symmetrical *cis*-2 bisadduct **8** in 48% yield. Model compound **9** was prepared in a similar manner starting from 1,3-benzenedimethanol (**10**): DCC esterification with **6** followed by reaction of the resulting bismalonate **11** with C<sub>60</sub> in toluene in the presence of DBU and iodine gave **9** in an overall 25% yield. Treatment of **7** with CF<sub>3</sub>CO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O 1:1 afforded benzaldehyde **3**. It was obtained in 93% yield as an orange-red glassy product and its preparation was easily carried out on a gram scale. The condensation of **3** and **4** was performed in CHCl<sub>3</sub> at room temperature in the presence of BF<sub>3</sub>·Et<sub>2</sub>O (Fig. 1A). After 12 h, *p*-chloranil (tetrachlorobenzoquinone) was added to irreversibly convert the porphyrinogen to the porphyrin. The desired porphyrin **1** was isolated in

38% yield. Preparation of porphyrin **2** was first attempted under the classical conditions reported by Lindsey and co-workers [51,52]. Reaction of benzaldehyde **3** with pyrrole in CH<sub>2</sub>Cl<sub>2</sub> with CF<sub>3</sub>CO<sub>2</sub>H as catalyst followed by *p*-chloranil oxidation yielded unreacted **3** and polymers, and no trace of porphyrin **2** could be detected. However, **2** could be obtained by using the reaction conditions developed by Lindsey for the synthesis of sterically hindered porphyrins such as tetramesitylporphyrin [53,54]. A key feature of these conditions involves BF<sub>3</sub>-ethanol cocatalysis. The condensation of **3** and pyrrole was performed in CHCl<sub>3</sub> (commercial CHCl<sub>3</sub> containing 0.75% ethanol as stabilizer) at room temperature in the presence of BF<sub>3</sub>·Et<sub>2</sub>O. After 5 h, *p*-chloranil was added to irreversibly convert the porphyrinogen to the porphyrin. The desired tetraphenylporphyrin **2** was subsequently isolated in 12% yield by tedious chromatographic separations. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures. The <sup>1</sup>H-NMR spectra of **1** depicted at room temperature the presence of two conformers in a 1:1 ratio. Molecular modeling studies on compound **1** revealed that each fullerene group is located atop its bridging phenyl ring. Therefore due to the high barrier to rotation of the phenyl substituents on the porphyrin, two conformers are possible for **1**. Actually, the two carbon spheres in **1** could be in a *cis* or in a *trans* relative position (Fig. 3). Whereas the two porphyrin H-meso are equivalent in the *trans* conformer, they are non-equivalent in the *cis* one. As expected, three singlets in a 1:2:1 ratio are observed at δ 10.20, 10.23, and 10.27 ppm, respectively, for the H-meso in the 1:1 mixture of conformers. Furthermore, the four methyl groups on the porphyrin are equivalent two to two in both conformers and the expected four singlets are clearly observed (δ 2.60, 2.63, 2.64, and 2.67 ppm) in the <sup>1</sup>H-NMR spectrum. A variable-temperature NMR study showed a clear coalescence at 125°C. By monitoring the coalescence of the porphyrin H-meso, the free energy barrier for the conformational equilibrium was calculated as Δ*G*<sup>‡</sup> = 85 kJ/mol. A sharp symmetric spectrum could not be obtained below the limit of heating, however the observed perfectly reversible narrowing of all the peaks unambiguously shows that a dynamic effect does occur. This *cis/trans* isomerism can be related to the diastereomerism observed for some terphenyl systems [55,56]. The characterization of **2** was also complicated since it appeared as a mixture of several conformers in slow equilibrium on the NMR time scale at room temperature, however all expected sets of signals are clearly observed. In tetraphenylporphyrin **2**, due to the fact that each fullerene group is located to one side of the plane of its bridging phenyl ring, free rotation of the four phenyl substituents on the porphyrin is required for the obtention of a sharp symmetric NMR spectrum. A variable-temperature study (CDCl<sub>2</sub>CDCl<sub>2</sub>, 400 MHz) showed a perfectly reversible narrowing of all the peaks at 125°C, however a sharp spectrum could not be obtained below the limit of

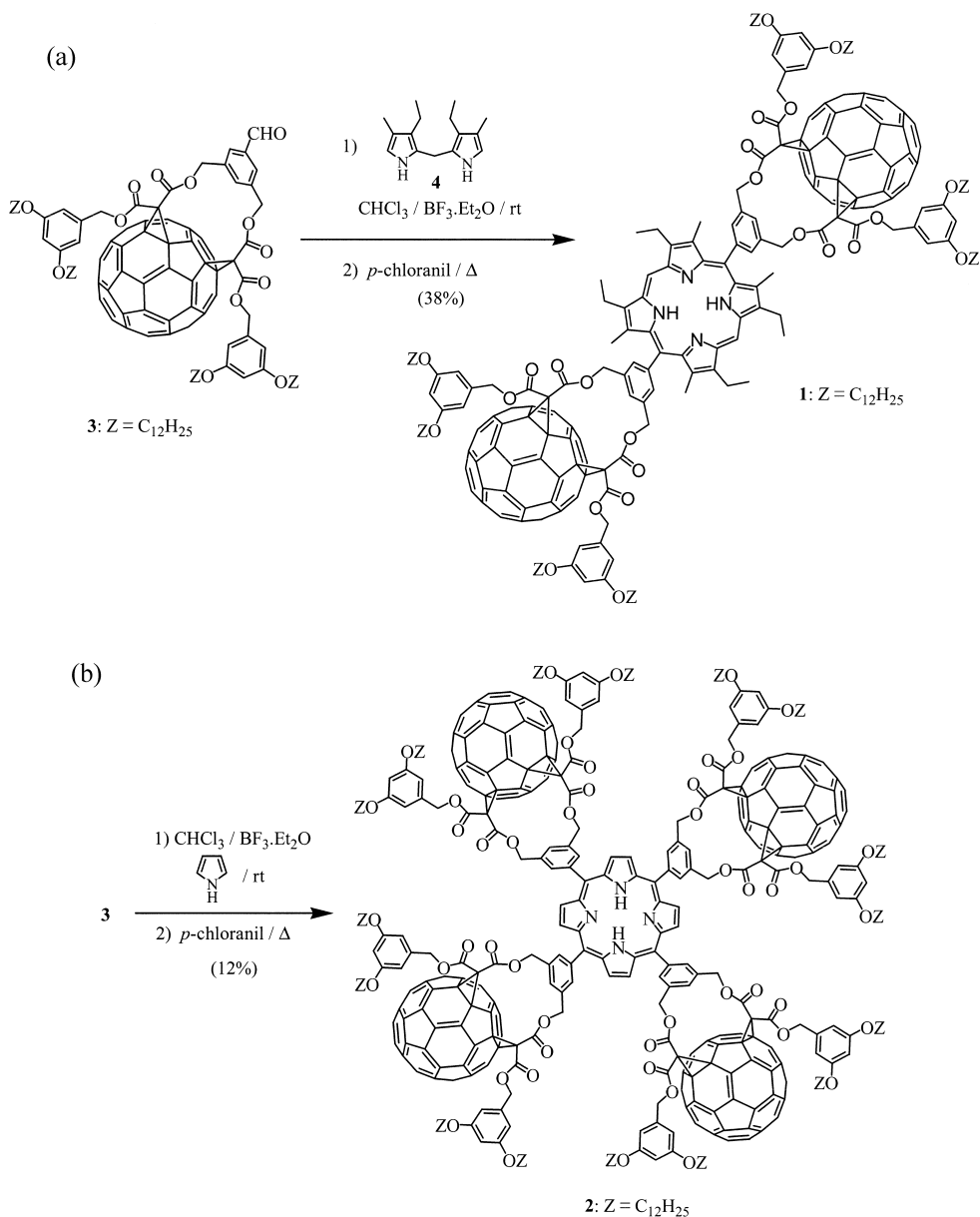
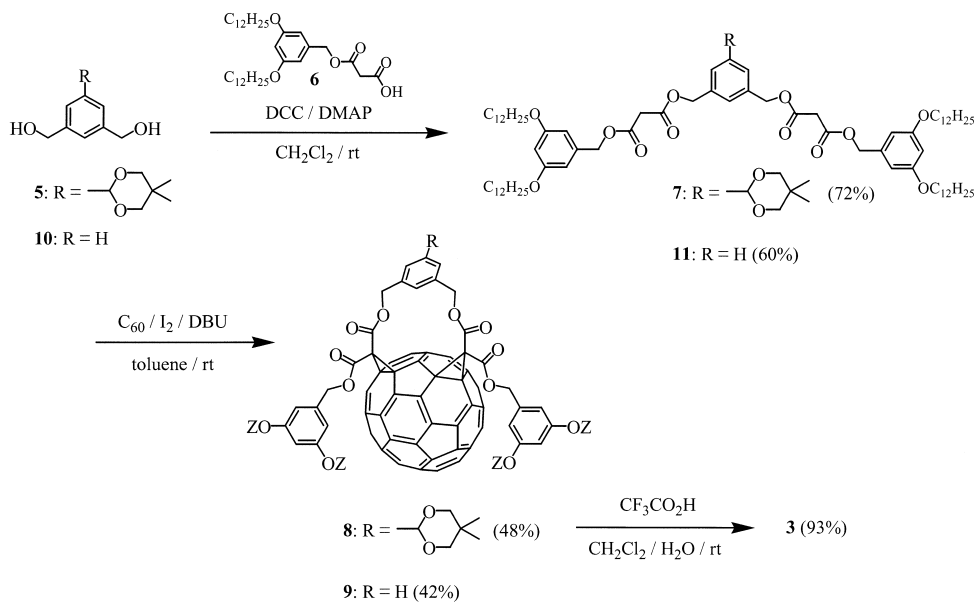


Fig. 1. (A) Preparation of porphyrin **1**. (B) Preparation of porphyrin **2**.

heating. Nevertheless, this NMR study unambiguously showed that a dynamic effect occurs.

The electrochemical investigations on porphyrins **1** and **2** were carried out by cyclic voltammetry (CV) in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> on a glassy C-electrode and the results are summarized in Table 1. The following porphyrins lacking the fullerene moieties were used for comparison purposes: 5,15-bis(3,5-di-*tert*-butylphenyl)-3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-porphyrin (**12**) [57] and *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (**13**) [58].

The redox potential of the first oxidation of the porphyrin moiety in **1** and **2** appears to be significantly more anodic ( $\Delta E \approx 100$  and 175 mV, respectively) than for the corresponding model porphyrins **12** and **13**, respectively. This observation could be related to the strong electron-withdrawing effect of the fullerene substituents, which could substantially destabilize the first oxidated state of the porphyrin moiety. However, solvation effects resulting from the presence of the surrounding fullerene groups could also be at the origin of the observed potential shift. For the reductions, **1**, **2** and model compound **9** showed a

Fig. 2. Preparation of  $C_{60}$ -benzaldehyde **3**.

similar behavior totally consistent with previously reported data for fullerene *cis*-2 bis-adducts [47–49]. For both **1** and **2**, all the fullerene subunits behave as independent redox centers. For compound **1**, the reduction potentials are shifted to more negative values ( $\Delta E \approx 40$  mV for the first reduction and 80 mV for the second one) when compared to fullerene derivative **9**. Those observations as well as the observed shift for the first oxidation of the porphyrin moiety in **1** seems to indicate that there are some interactions between the porphyrin moiety and the fullerene substituents in **1**. In contrast, although the  $C_{60}$  substituents apparently influenced significantly the redox properties of the porphyrin moiety in **2**, those of the fullerene subunits seem to remain unchanged by the porphyrin in **2**. The influence of the porphyrin on the reduction potentials of the two fullerene substituents observed for compound **1** could not be seen for **2** since it is

somehow diluted by the increased number of surrounding fullerene subunits.

Preliminary luminescence measurements indicate that the porphyrin emission in **1** and **2** is totally quenched at room temperature by the surrounding fullerene subunits. The shift observed by CV for the redox properties as well as the absence of emission seem to indicate some electronic interactions among the different components in the ground state as well as in the excited states for both **1** and **2**.

### 3. Fullerene-functionalized dendrimers

In light of their unique structures and properties, dendrimers have attracted increasing attention in the past decade [59] and the use of dendrimer building blocks for the self-assembly of larger nano- and mesoscopic supramolecular structures appears as an emerging area with unlimited possibilities for fundamental new discoveries and practical applications [59,60]. Dendrimers containing various electro- and photoactive chromophores have been prepared in order to explore influences of the microenvironment inside the macromolecule on the properties of the functional core [61,62]. On the other hand, because a dendrimer surface may contain multiple copies of a given functional group, it can be used for example as a platform for amplification of substrate binding [63,64] or as an antenna for light harvesting [65,66]. We report herein the preparation of new dendrimers with a bis(1,10-phenanthroline)copper(I) core and fullerene  $\pi$  chromophores at the periphery. We also report here the electrochemical and

Table 1

Redox characteristics of **1**, **2**, **9**, **12** and **13** observed by CV on a glassy C electrode in  $CH_2Cl_2 + 0.1$  M  $Bu_4NPF_6^a$

Compound	Reduction		Oxidation $E_1$
	$E_1$	$E_2$	
<b>1</b>	-1.07	-1.45 <sup>b</sup>	+0.43
<b>2</b>	-1.03	-1.36 <sup>b</sup>	+0.695
<b>9</b>	-1.03	-1.37 <sup>b</sup>	%
<b>12</b>	-1.85	-2.30 <sup>b</sup>	+0.33
<b>13</b>	-1.66	-2.00	+0.52

<sup>a</sup> Values for  $(E_{pa} + E_{pc})/2$  [V vs.  $Fc/Fc^+$ ].

<sup>b</sup> Peak potential values at a scan rate of  $0.1$  V  $s^{-1}$ , irreversible process.

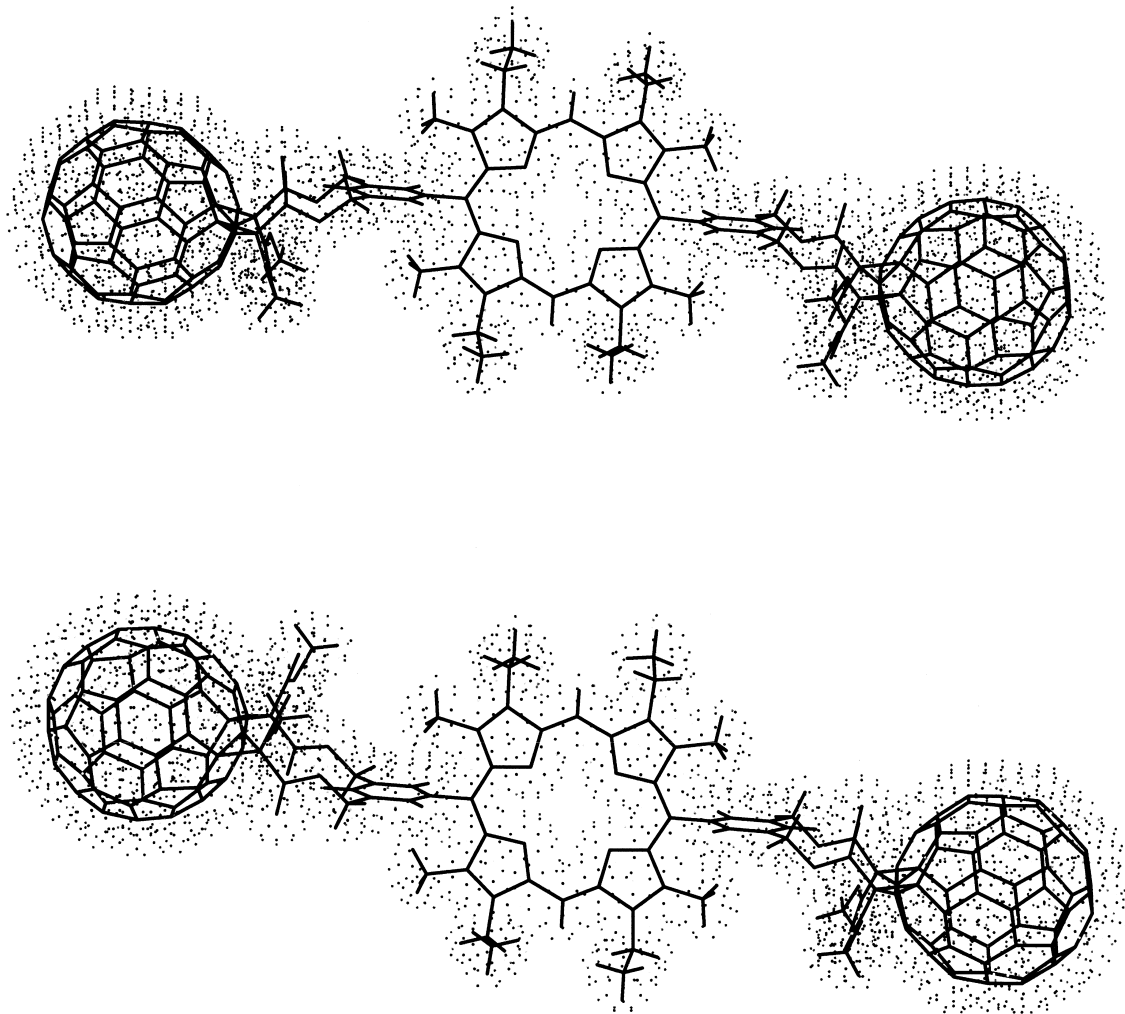


Fig. 3. Molecular models of the two conformers of compound **1** (the four dodecyloxyphenyl groups have been omitted for clarity).

photophysical behavior of these dendrimers and show how the surrounding fullerene-functionalized dendritic branches are able to isolate the central Cu(I) complex.

The fullerene-functionalized dendritic branches  $G_n\text{CO}_2\text{H}$  were prepared as depicted in Fig. 4. Reaction of  $G_1\text{CO}_2\text{H}$  [67,68] with diol **14** under esterification conditions using DCC, 1-hydroxybenzotriazole (BtOH) and 4-dimethylaminopyridine (DMAP) led to the *t*-butyl-protected dendron  $G_2\text{CO}_2t\text{-Bu}$  of second generation in 90% yield. Subsequent treatment with  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CH}_2\text{Cl}_2$  afforded  $G_2\text{CO}_2\text{H}$  in high yield (99%).

Esterification of  $G_2\text{CO}_2\text{H}$  with diol **14** (DCC/DMAP/BtOH) gave  $G_3\text{CO}_2t\text{-Bu}$  in 84% yield and subsequent hydrolysis of the *t*-butyl ester group under acidic conditions afforded the third generation carboxylic acid  $G_3\text{CO}_2\text{H}$ . Diol **15** was prepared according to the literature procedure [69] and allowed to react with the dendrons  $G_1\text{--}3\text{CO}_2\text{H}$  under DCC-mediated esterification conditions

to give the corresponding ligands L1–3 (Fig. 5). The copper(I) complexes  $(\text{L}1\text{--}3)_2\text{Cu}$  were obtained by treatment of the corresponding ligands L1–3 (1 equiv.) with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$  (0.6 equiv.).  $(\text{L}1\text{--}3)_2\text{Cu}$  were thus formed in good yields; however, due to difficulties encountered during their purification, the isolated yields were low (56% for  $(\text{L}1)_2\text{Cu}$ , 35% for  $(\text{L}2)_2\text{Cu}$  and 33% for  $(\text{L}3)_2\text{Cu}$ ). Partial decomposition of the complexes was observed on  $\text{Al}_2\text{O}_3$  (also on  $\text{SiO}_2$ ); effectively, a part of the product stuck all along the column (this could be easily observed because of the compound's dark red color) and could not be eluted any more. Model compound  $(\text{L}0)_2\text{Cu}$  was prepared in a similar manner from diol **15** (Fig. 5).

Whereas the coordination of the ligands L1–3 to the copper(I) cation could not be easily observed by apparition of the metal-to-ligand charge transfer (MLCT) band characteristic of bis(2,9-dialkyl-1,10-phenanthroline)-copper(I) derivatives at ca. 456 nm [70,71] since it is

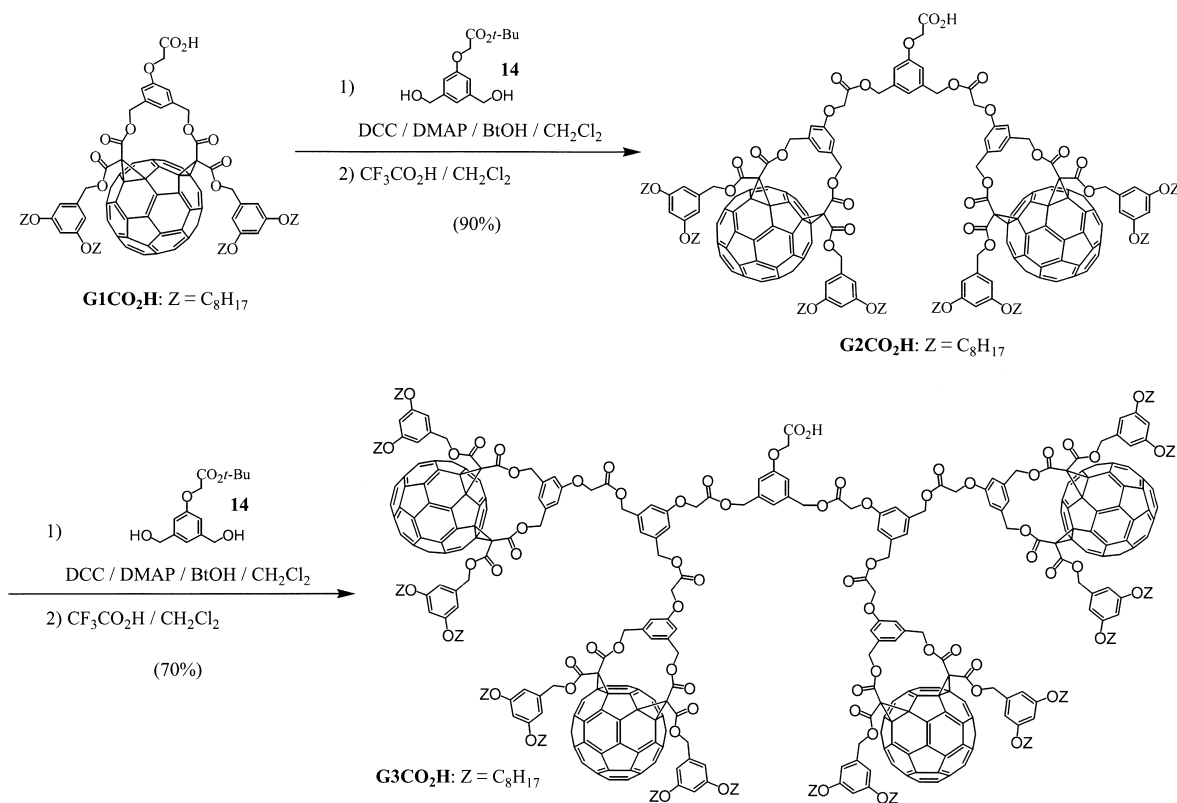


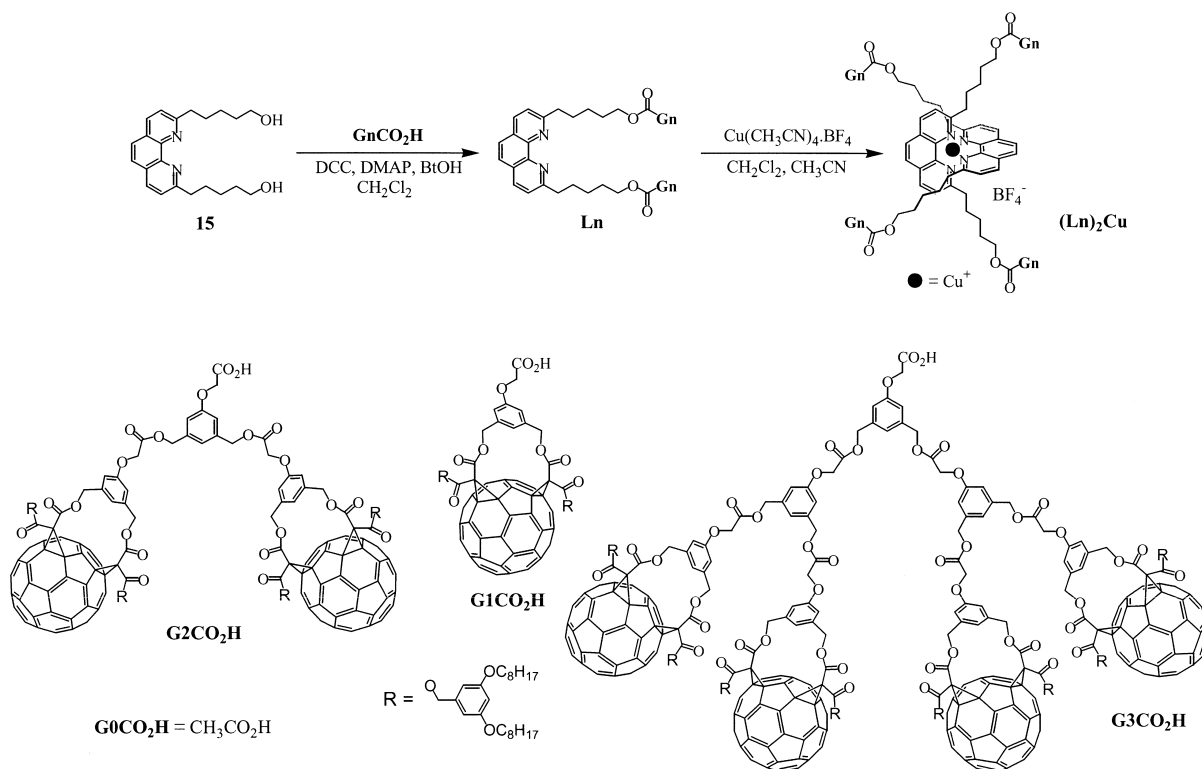
Fig. 4. Preparation of dendrons with peripheral fullerene units.

masked by the fullerene absorption in this region, the <sup>1</sup>H-NMR spectra of (L1–3)<sub>2</sub>Cu provide good evidence for their formation. Effectively, the methylene group directly attached to the phenanthroline core observed at ca. 3.2 ppm in the ligands L1–3 is shifted to ca. 2.6 in the corresponding complexes (L1–3)<sub>2</sub>Cu. This particular behavior is highly specific for such copper(I) complexes [72] and is the result of the ring current effect of one phenanthroline subunit on the 2,9-substituents of the second one in the complex. Furthermore, the FAB-MS confirmed the structure of (L1)<sub>2</sub>Cu with signals at  $m/z = 7872.7$  and  $3967.6$  corresponding to  $[M-\text{BF}_4^-]^+$  (calc. for C<sub>532</sub>H<sub>400</sub>O<sub>60</sub>N<sub>4</sub>Cu: 7872.6) and  $[M-\text{L1}-\text{BF}_4^-]^+$  (calc. for C<sub>266</sub>H<sub>200</sub>O<sub>30</sub>N<sub>2</sub>Cu: 3968.1), respectively. In the FAB-MS spectra of (L2)<sub>2</sub>Cu, only the peak corresponding to  $[M-\text{L2}-\text{BF}_4^-]^+$  could be observed at  $m/z = 7908.1$  (calc. for C<sub>530</sub>H<sub>392</sub>O<sub>66</sub>N<sub>2</sub>Cu: 7908.5). It should be pointed out that no peaks corresponding to defected dendrons were observed in the FAB-mass spectra of (L1–2)<sub>2</sub>Cu, thus providing clear evidence for their monodispersity. In the FAB-MS of (L3)<sub>2</sub>Cu, no characteristic peak could be observed. Due to the presence of the 64 surrounding long alkyl chains, (L3)<sub>2</sub>Cu aggregates strongly and high energy is required for dissociation during FAB-MS analysis, therefore fragmentation occurs, especially on the fragile

benzylic ester functions; furthermore its molecular mass is quite high (31 601.8). Nevertheless, the NMR and UV/Vis data obtained for (L3)<sub>2</sub>Cu and comparison with (L1–2)<sub>2</sub>Cu provide very good evidence for the proposed structure.

The electrochemical investigations on GnCO<sub>2</sub>tBu and (Ln)<sub>2</sub>Cu were carried out by CV in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> on a glassy C-electrode and the results are summarized in Table 2.

Compound G1CO<sub>2</sub>tBu shows the characteristic behavior previously reported for fullerene *cis*-2 bis-adducts [47–49]. Whereas the first reduction, which occurs at  $-1.07$  V vs. Fc/Fc<sup>+</sup>, is reversible, the second reduction observed at ca.  $-1.4$  V is irreversible. It has actually been shown that the second electron transfer in *cis*-2 derivatives is followed by a chemical reaction [47–49]. For the reductions, similar results were obtained with the dendrimers of higher generations G2–3CO<sub>2</sub>tBu and (L1–3)<sub>2</sub>Cu. Thus suggesting that all the peripheral fullerene subunits behave as independent redox centers in all compounds. The Cu<sup>I</sup>/Cu<sup>II</sup> oxidation potential in (L1)<sub>2</sub>Cu remains unchanged when compared to model compound (L0)<sub>2</sub>Cu showing also that there is no particular intramolecular electronic communication between the central copper(I) complex and the four surrounding fullerene units in (L1)<sub>2</sub>Cu. The amplitude of

Fig. 5. Preparation of the copper(I) complexes (L0–3)<sub>2</sub>Cu.

the fullerene-centered reduction is expected to be four times larger than that of the Cu-centered oxidation. Interestingly, however, the amplitude of the oxidation peak in (L1)<sub>2</sub>Cu is smaller than expected. In addition, the metal-centered oxidation became irreversible, thus indicating decrease of the electron transfer kinetic as previously

Table 2

Redox characteristics of G1–3CO<sub>2</sub>*t*Bu and (L0–3)<sub>2</sub>Cu observed by CV on a glassy C electrode in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub><sup>a</sup>

Compound	Reduction		Oxidation
	$E_1$	$E_2$	$E_1$
G1CO <sub>2</sub> <i>t</i> Bu	–1.07	–1.45 <sup>b</sup>	+1.2 <sup>b</sup>
G2CO <sub>2</sub> <i>t</i> Bu	–1.07	–1.45 <sup>b</sup>	+1.1 <sup>b</sup>
G3CO <sub>2</sub> <i>t</i> Bu	–1.08	–1.45 <sup>b</sup>	+1.1 <sup>b</sup>
(L0) <sub>2</sub> Cu	–2.20 <sup>b,c</sup>		+0.60
(L1) <sub>2</sub> Cu	–1.08	–1.39 <sup>b</sup>	+0.60 <sup>d</sup>
(L2) <sub>2</sub> Cu	–1.08	–1.43 <sup>b</sup>	Not observed
(L3) <sub>2</sub> Cu	–1.07	–1.40 <sup>b</sup>	Not observed

<sup>a</sup> Values for  $(E_{pa} + E_{pc})/2$  [V vs. Fc/Fc<sup>+</sup>] at a scan rate of 0.1 V s<sup>–1</sup>.

<sup>b</sup> Peak potential values at a scan rate of 0.1 V s<sup>–1</sup>, irreversible process.

<sup>c</sup> Reversible for  $v > 0.5$  V s<sup>–1</sup>.

<sup>d</sup> Poor resolved signal of small amplitude.

observed for other electroactive cores in dendrimers [60,61]. This suggests that the bulky fullerene subunits around the Cu center partially prevent its approach on the electrode surface and, as a result, the oxidation at the central core could not be completed in the time scale of the CV measurement. Consistent with this, the electrochemical oxidation of the Cu site could no longer be observed in dendrimers of the highest generations (L2)<sub>2</sub>Cu and (L3)<sub>2</sub>Cu. The central electroactive site appears to be totally inaccessible since it is isolated by the bulkier surrounding dendrimer structures. This observation is in full agreement with the molecular modeling studies which show that the interior of the dendrimer in (L2)<sub>2</sub>Cu and (L3)<sub>2</sub>Cu is virtually inaccessible to external contacts.

The absorption spectra of all the dendrimers (L1)<sub>2</sub>Cu, (L2)<sub>2</sub>Cu, and (L3)<sub>2</sub>Cu in CH<sub>2</sub>Cl<sub>2</sub> coincide with the sum of the corresponding component units, showing no appreciable ground state electronic interactions among them. The increasing number of fullerene units around the Cu(I)-complexed core implies a more and more extended shielding of the central core from the incident light. Upon selective excitation of the peripheral C<sub>60</sub> units at 600 nm, fullerene fluorescence is observed for all dendrimers (L1–3)<sub>2</sub>Cu; the corresponding emission quantum yield and excited state lifetimes are identical, within the experimental error, to those of the corresponding dendrimeric subunits



GnCO<sub>2</sub>*t*-Bu. Despite the fact that selective excitation of the [Cu(phen)<sub>2</sub>]<sup>+</sup>-type dendrimer central core is not possible, clear evidence of the luminescence quenching of such a moiety can be obtained. For instance by exciting (L1)<sub>2</sub>Cu at 456 nm, although the light partition is about 40% (core) and 60% (fullerenes), the MLCT emission of the central core is dramatically quenched in a steady-state experiment. Analogous patterns are shown by (L2–3)<sub>2</sub>Cu, although the light partition at 456 nm is less favorable for the central core because of the above mentioned shielding effect (for (L2)<sub>2</sub>Cu ca. 20% of the incident light is able to reach the central core; for (L3)<sub>2</sub>Cu this value is ca. 10%). An energy level diagram reporting all the low-lying electronic levels is depicted in Fig. 6. The lowest singlet (<sup>1</sup>Gn) and triplet (<sup>3</sup>Gn) centered on the peripheral fullerene fragments and the lowest MLCT excited state of the Cu(I)-complexed central core (<sup>MLCT</sup>GnCu).

The energy values were obtained from corrected luminescence band maxima at 77 K or, when not available as in the case of <sup>3</sup>Gn (phosphorescence from C<sub>60</sub> and its derivatives has been rarely reported and only in matrices below 5 K or, at 77 K, in the presence of heavy atom containing solvents), from theoretical calculations. It is noteworthy that a new low-energy electronic level is made available in the supramolecular array, namely the charge separated state Cu<sup>+</sup>–Gn<sup>–</sup> located at 1.68 eV, as deduced from the electrochemical data [73]. In principle, the quenching of the MLCT excited state (positioned at 1.85 eV) can occur via three pathways: (i) energy transfer to the fullerene centered singlet <sup>1</sup>Gn ( $\Delta G = -0.10$  eV) [73]; (ii) energy transfer to the fullerene centered triplet <sup>3</sup>Gn ( $\Delta G = -0.45$  eV); (iii) electron transfer to the charge separated state ( $\Delta G = -0.17$  eV). We believe that electron transfer [process (iii)] is not the prevailing phenomenon for at least two reasons: (a) it does not take place from <sup>1</sup>Gn (no

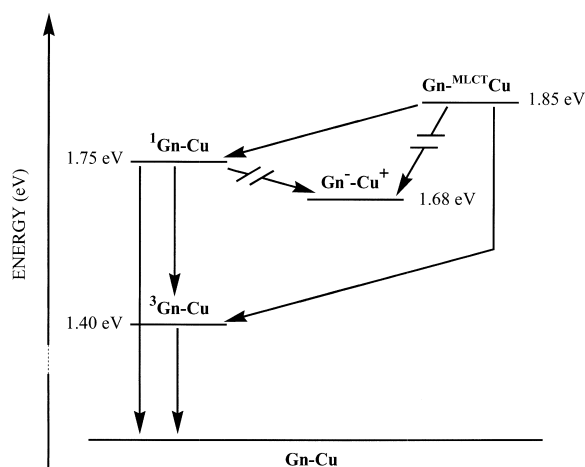


Fig. 6. Energy level diagram describing the excited state deactivation pathways and the intercomponent energy transfer processes in the dendrimers.

quenching of the fluorescence of the fullerene moiety is observed), although a similar thermodynamic driving force ( $\Delta G = -0.07$  eV) would be involved; (b) the quenching of the central core occurs also at 77 K, but electron-transfer in a rigid matrix is usually blocked if not exothermic by at least 0.6–0.7 eV [74,75] (in our case  $\Delta G = -0.17$  eV, Fig. 6). Further experiments are still underway in order to have a better insight about this issue.

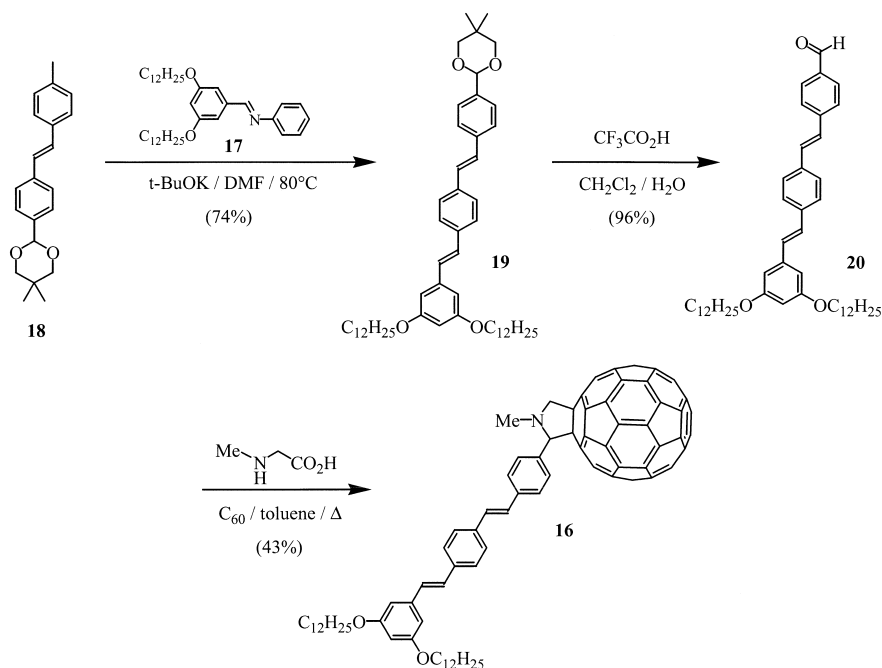
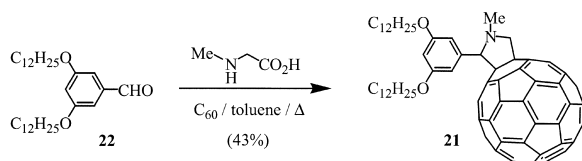
In conclusion, due to the increasing number of surrounding fullerene subunits in (L1)<sub>2</sub>Cu to (L3)<sub>2</sub>Cu, there is less and less light available for the core, relative to the periphery, and the small portion of light energy able to excite the central Cu(I) complex is returned to the external fullerenes by energy transfer. Therefore, one can conclude that the Cu(I) central core is buried in a kind of dendritic black box.

#### 4. A fullerene–oligophenylenevinylene derivative

Photovoltaic devices using thin films of interpenetrating bicontinuous networks of C<sub>60</sub> itself or a C<sub>60</sub> 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 [76–82]. 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 [83]. In such a way, any problems arising from bad contacts at the junction are avoided. In this context, we describe the preparation of the fullerene–oligophenylenevinylene hybrid **16** and its utilization for the construction of a solar energy conversion system. The synthesis of compound **16** is depicted in Fig. 7.

Benzaldimine **17** was subjected to the Siegrist reaction [84] with stilbene **18** to give protected trimer **19** in 74% yield. Treatment of **19** with CF<sub>3</sub>CO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (1/1) afforded aldehyde **20** in 96% yield. The functionalization of C<sub>60</sub> was based on the 1,3-dipolar cycloaddition [85] of the azomethine ylide generated in situ from **20**. The reaction of C<sub>60</sub> with **20** in the presence of an excess of *N*-methylglycine (sarcosine) in refluxing toluene afforded fulleropyrrolidine **16** in 43% yield (or 62% based on the non-recovered C<sub>60</sub>). Model compound **21** was prepared in a similar manner from aldehyde **22** by reaction with C<sub>60</sub> and sarcosine in refluxing toluene (Fig. 8).

The UV-vis spectrum of **16** corresponds to the sum of the spectra of its two components and shows the characteristic absorptions of a fulleropyrrolidine derivative at

Fig. 7. Preparation of compound **16**.Fig. 8. Preparation of model compound **21**.

254, 430, and 702 nm as well as the diagnostic oligophenylenevinylene (OPV) band at 363 nm. Thus indicating that there are no significant interactions between the two chromophores in the ground state. Preliminary luminescence measurements show a strong quenching of the OPV fluorescence in **16**. Charge transfer is expected to occur and compound **16** appears as a potential candidate for the preparation of a photovoltaic cell. The electrochemical properties of **16**, **19** and **21** were investigated by

CV. All the experiments were performed at room temperature in *o*-dichlorobenzene solutions, containing tetra-*n*-butylammonium hexafluorophosphate (0.05 M) as supporting electrolyte, with glassy carbon as the working electrode, a Pt wire counter electrode and Ag/AgCl as the reference electrode. Potential data are collected in Table 3.

The fullerene–OPV hybrid compound **16** shows three reversible reduction peaks in the cathodic direction and a chemically irreversible oxidation peak in the anodic part. As shown by the comparison with model compounds **19** and **21**, the OPV and fulleropyrrolidine oxidation waves could not be clearly distinguished because both constituents are oxidized at similar potentials. For the reductions, both  $C_{60}$  derivatives **16** and **21** essentially retain the electronic properties of  $C_{60}$  and, as typically observed for most  $C_{60}$  derivatives [86,87], the observed reduction potentials of both **16** and **21** are shifted to more negative values when compared to those of unsubstituted  $C_{60}$ . The

Table 3

Redox characteristics of  $C_{60}$ , **16**, **19** and **21** observed by CV on a glassy C electrode in *o*-dichlorobenzene + 0.05 M  $Bu_4NPF_6$ <sup>a</sup>

Compound	Reduction			Oxidation	
	$E_1$	$E_2$	$E_3$	$E_1$	$E_2$
$C_{60}$	−0.552	−0.928	−1.363		
<b>16</b>	−0.654	−1.019	−1.534	+1.354 <sup>b</sup>	%
<b>19</b>				+1.305 <sup>b</sup>	+1.520 <sup>b</sup>
<b>21</b>	−0.643	−1.009	−1.520	+1.389 <sup>b</sup>	+1.550 <sup>b</sup>

<sup>a</sup> Values for  $(E_{pa} + E_{pc})/2$  [V vs. Ag/AgCl] at a scan rate of 0.1 V s<sup>−1</sup>.

<sup>b</sup> Peak potential values at a scan rate of 0.1 V s<sup>−1</sup>, irreversible process.

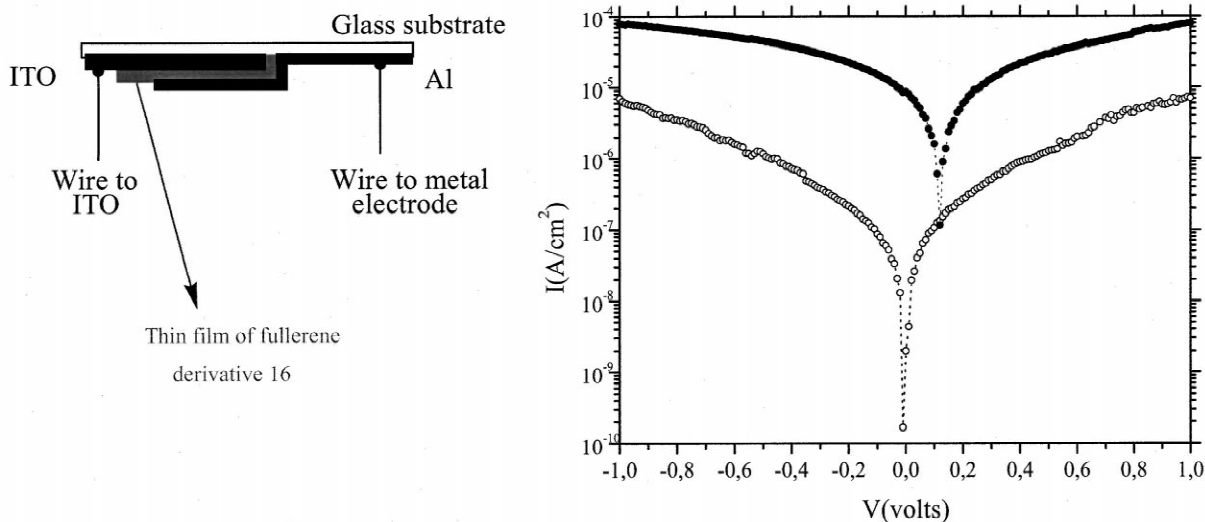


Fig. 9. Structure of the photovoltaic cell and current–voltage characteristics of the device in the dark (○) and under  $5 \text{ mW cm}^{-2}$  illumination (400 nm) (●).

comparison of the  $E_{1/2}$  potentials of **16** and **21** shows that the reduction potentials of **21** are all slightly shifted to more negative values by 10–14 mV. This shift could result from the interactions between the donating OPV moiety and the accepting  $\text{C}_{60}$  spheroid. This is actually in good agreement with the results recently reported for ferrocenyl fulleropyrrolidines [88] and for dimethylaniline-substituted dithienylethyl fulleropyrrolidines [89].

The  $\text{C}_{60}$ -OPV hybrid compound has been used for the construction of a solar energy conversion system and the device structure is schematically depicted in Fig. 9. Thin films of the  $\text{C}_{60}$ -OPV derivative **16** were spin cast, on a glass substrate coated with indium-tin-oxide (ITO), from weight 4% chloroform solution. The Al electrode was vacuum evaporated on the films to a thickness of 100 nm. Typical  $I$ - $V$  curves (using ITO as positively and Al as negatively biased electrodes) measured under dark and under light (400 nm,  $5 \text{ mW/cm}^2$ ) are presented in Fig. 9.

Under the light the device shows clear photovoltaic behavior with open-circuit voltage of around 0.2 V and short-circuit current density  $10 \text{ } \mu\text{A/cm}^2$  corresponding to collecting efficiency of 1%. Although we do not know the exact reason of the high dark current under reverse bias, we believe it causes relatively low collection efficiency and open-circuit voltage.

## 5. Conclusions

Our recent progress in the chemistry of  $\text{C}_{60}$  allowed us to prepare several fullerene derivatives covalently bound to other chromophores. These systems provided entry into

intramolecular processes such as electron and energy transfer. The synthesis of  $\text{C}_{60}$  polyadducts with well defined three-dimensional structure provides versatile building blocks for the preparation of porphyrin–fullerene derivatives with unusual stereochemical and electronic properties as well as for the synthesis of phenanthroline ligands substituted with fullerene-functionalized dendritic wedges and their copper(I) complexes. As well as the undeniable aesthetic appeal of all these exotic compounds, we have shown that the combination of  $\text{C}_{60}$  with other photo- and electro-active components is able to perturb the ground-state and excited-state properties of the individual species, giving rise to novel properties. Finally, a fullerene-OPV hybrid compound has been synthesised in order to provide a molecular approach to photovoltaic conversion, and to prevent the morphology problems resulting from the phase separation in donor-acceptor composites. The light-collecting and energy-conversion efficiencies of the molecular photovoltaic system is not yet optimized, and further improvements could be expected by utilization of new fullerene derivatives with a strong absorption in the visible range and able to achieve very fast charge separation and slow charge recombination.

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