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# Weak intrinsic charge transfer complexes: A new route for developing wide spectrum organic photovoltaic cells

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Solar emission extends in the near IR and one of the main issues in designing organic solar cells resides in extending the response into the near IR. Here we show that this may be achieved by making intimate interpenetrated networks of  $C_{60}$  and Zn-phthalocyanine (Zn-Pc) in the solid. Various spectroscopic investigations of co-sublimated thin films of  $C_{60}$  and Zn-phthalocyanine give indeed ample evidence of the existence of a weak charge transfer (CT) state at 1.4 eV, which quenches the photoluminescence of both molecules. The films produced by co-sublimation undergo to a spinodal decomposition producing domains prevalently constituted by Zn-Pc in contact with domain prevalently of  $C_{60}$ . The domains size depends on the deposition conditions (rate, stoichiometry, and substrate temperature) forming a percolating 3D network. The separation in different domains is confirmed by the observation of two overlapping peaks, in the resonant Raman spectrum, that correspond to the  $A_g(2)$  pinch mode (C = C double bond stretching) for pristine  $C_{60}$  and for a partially ( $\sim 0.25e^-$ ) doped one. This indicates that only those donor molecules at the grain boundary, which are in contact with  $C_{60}$ , give rise to a renormalized new CT ground state. Photocurrent measurements of interpenetrated networks of  $C_{60}$  and Zn-Pc show a linear dependence with respect to the incident light as a consequence of direct absorption within the CT state. The CT state favors the charge separation between the two

components, when it is inserted as interface in the organic photovoltaic  $p$ - $n$  junction thus increasing the efficiency of the device.

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## I. INTRODUCTION

The last 20 years have seen a large effort in the investigation of "plastics" organic materials as new materials for optoelectronics and electronics. The low cost and the high versatility of organic compound because of the possibility of tuning their optical and electrical properties by chemical tailoring are the base of such a wide interest from both the applied and basic research. In several cases silicon and other inorganic materials have been replaced by conjugated molecules in electronic and electro-optical devices like light emitting diodes (LED) for color displays <sup>1-3</sup> or in the active components for xerography<sup>4</sup> and a large effort is presently devoted in developing all organic electronic devices <sup>5</sup> like photodiodes, field effect transistors (FET) <sup>8-15</sup> Among the many possible acceptor (A)-donor (D) pairs we have selected C<sub>60</sub> (Fig.1) and Zn-phthalocyanine (Zn-Pc) (Fig.2), respectively.

C<sub>60</sub> attracted the interest of researchers, as soon as becoming available in gram size <sup>16</sup> superconductivity <sup>17</sup> as well as ferromagnetism <sup>18</sup> was observed in fullerenes. Moreover, C<sub>60</sub> as well as all fullerenes and fullerene derivatives, is one of few organic compounds that behave as an  $n$ -type (A) material. The limited number of organic molecules that act as  $n$ -type materials is one of the most severe limitations in the development of organic based electronics. Mainly for this reason we have used C<sub>60</sub>.

Metal-phthalocyanines (M-Pc), used since the beginning of the 20th century as dyes in the textile industry, have gained a large interest in the organic based electronic devices like photoreceptors in xerography and components of laser printer drums <sup>4,19,20</sup>

Phthalocyanines have been also studied successfully as  $p$ -type materials in organic solar cells <sup>8,9,12</sup> The complementarity of their visible (VIS) absorption spectra as well as of their electron affinity nature (i.e.,  $n$ -type C<sub>60</sub> and  $p$ -type Zn-Pc), makes them two natural candidates for developing  $p$ - $n$  organic photovoltaic devices <sup>12,15</sup> With this perspective, we have investigated the interaction of the two molecules in the solid. Films of Zn-Pc and C<sub>60</sub> were deposited under highly controlled conditions in ultra high vacuum (UHV) and studied using different methods: optical absorption, photoluminescence, Raman spectroscopy, and photocurrent measurements. Kessler <sup>21</sup> suggested that the relative energy positions of the band offset between the HOMO of M-Pc and the LUMO of C<sub>60</sub>, derived from UPS

photoelectron measurement, can favor charge separation between the two molecules. In this paper we experimentally demonstrate that the ground state is an intrinsic CT state with partial electron transfer from Zn-Pc to C<sub>60</sub>. Generation of free charge carriers by exciting the renormalized CT ground state in the infrared, obtained by photoconductivity measurements, is also reported. This result suggests that those free carriers are formed by direct fission of the exciton associated to the charge transfer state. The feasibility of such a process opens the possibility to improve the efficiency of organic solar cells also extending their photovoltaic response to the near infrared (NIR) spectral region.

## II. EXPERIMENT

The materials were purified by several runs of vacuum sublimation in a three-zone furnace using as starting materials a 99.99% C<sub>60</sub> fullerene (SES) and Zn-Pc (Kodak) previously purified by recrystallization. Thin films were obtained by sublimation of high purity compounds, in molecular beam deposition (Organic-MBD) conditions. Independently controlled effusion Knudsen-type cells, especially designed for organic molecules allowing good control of the growth rate conditions (time stability and reproducibility), were used as molecular beam sources. Film deposition has been accomplished in UHV ambient by means of a three chambers system especially designed for growth and *in situ* characterization of organic thin films. Base pressure in the growth chamber before evaporation was  $3 \times 10^{-10}$  mbar and during the evaporation was better than  $2 \times 10^{-9}$  mbar. Growth by means of O-MBD is a powerful technique for an accurate monitoring of the deposition parameters like substrate temperature, deposition rate, thickness, and composition ratio. This allows to control the architecture of the film by generating submonolayers, heteromultilayers, and co-sublimated layers on different substrates (metals, quartz, glass, and ITO glass).

The rate of evaporation was 0.1–0.2 Å/s and the films thickness, measured by a quartz thickness monitor, ranged in the interval 30–200 nm; a calibration procedure of the thickness monitor has been obtained by using an atomic force microscope (AFM). The residual atmosphere during the growth was monitored by a quadrupole gas analyzer (RIAL qm 130).

NIR-VIS absorption measurements have been performed by using a FT interferometer (Bruker IFS 88) with a Si detector in the region from 1 to 2.1 eV and a grating monochromator spectrometer (JASCO 500) for the spectral region from 1.4 eV to 3.6 eV.

Luminescence spectra in the NIR range between 0.75 and 1.2 eV were measured by using a modified FT interferometer (Bruker RFT 100) equipped with a liquid nitrogen cooled Ge detector, while in the visible we used a micro-Raman spectrometer (Renishaw 1000).

Measurements were performed both in air and in vacuum by exciting with both the 488 and 514 nm Ar<sup>+</sup> laser lines.

NIR excited Raman scattering measurements were performed by using a Bruker RFT 100 coupled with a cw diode pumped Nd-YAG laser at 1064 nm (1.16 eV). Because of the low scattering cross section for thin films, very long integration times, of the order of 1–2 h, were needed. Raman measurements in the visible have been performed by using a micro-Raman spectrometer (Renishaw 1000). HeNe at 632.8 nm (1.96 eV) and Ar<sup>+</sup> 514.5 and 488 nm (2.41 and 2.54 eV) laser line were used as excitation sources. NIR-VIS-UV absorption, luminescence, and Raman measurements have been performed on several films deposited on quartz and glass substrates. All the results discussed in this paper are referred to films deposited at room temperature at the same deposition rate (6 Å/min).

*I*-*V* measurements have been performed by using a computer controlled Keithley source-measure unit mod. 236. The measurements reported in this paper have been obtained by illuminating the devices with a cw diode pumped Nd-YAG laser at different power intensities. We have investigated two *p*-*n* junctions with different sandwich structures between a patterned ITO substrate and a Al electrodes: (a) a double-layer device constituted by ITO/Zn-Pc (75 nm)/C<sub>60</sub> (90 nm)/Al, and (b) a triple-layer device formed by intercalating among the *p*- and *n*-type components a 30 nm thick layer obtained by co-sublimation of Zn-Pc + C<sub>60</sub> (50%+50% of relative thickness) [ITO/Zn-Pc(60 nm)/Zn-Pc + C<sub>60</sub>(30 nm)/C<sub>60</sub>(75 nm)/Al].

### III. RESULTS

#### A. Absorption spectroscopy

The thin films absorption spectra of single components C<sub>60</sub> and Zn-Pc obtained by sublimation in UHV are reported in Fig.3. The C<sub>60</sub> absorption spectrum is characterized, in the VIS-UV range, by the weak bands that are associated to the forbidden HOMO-LUMO transition<sup>22</sup> The shape of these peaks does not depend significantly on the crystal structure and quality and consequently it is almost independent from the deposition condition. On the contrary, in the case of Zn-Pc, the shape of the visible absorption features (i.e., in the spectral region of the *Q* band), are indicative of the crystallographic

phase of the Zn–Pc <sup>23-28</sup> From the absorption spectra of the single component films of Zn–Pc we infer that Zn–Pc is in the  $\alpha$ -phase, as expected from the deposition conditions. The comparison of the absorption spectra of a co-sublimated film of Zn–Pc + C<sub>60</sub>, with those obtained from films of equivalent thickness of the single components sublimed in the same conditions (substrate temperature and rates), reveals clearly several differences (see Fig 3). As one would expect in the case of interacting systems, the spectrum of the co-sublimated film is not simply the weighted sum of the two spectra of the single components. In the co-sublimated film, the absorption features associated with C<sub>60</sub> do not change significantly with respect to those of pristine C<sub>60</sub> film deposited in the same conditions. The spectra of co-sublimated films, around the Q band transition, show features in between the amorphous and the  $\alpha$ -phase as can be deduced by the comparison with the large literature published on this material <sup>26-27</sup> It is possible to analyze the spectrum of the co-sublimated films in terms of different contributions by C<sub>60</sub>, Zn–Pc  $\alpha$ -phase and amorphous Zn–Pc. Moreover, the absorption spectrum of the co-sublimated film shows a long low energy tail in the near infrared region. Such a tail is not present either in the C<sub>60</sub> or in any possible crystalline as well as amorphous phase associated with Zn–Pc. In this spectral range, M–Pc shows a very weak singlet–triplet absorption induced by the relaxation of the selection rules due to the spin–orbit coupling of the heavy atom. Nevertheless, the absorption that we observe in the co-sublimated film is much more intense than what is expected for the singlet–triplet transition. It is possible to fit the spectrum by adding to the pristine components (C<sub>60</sub>, Zn–Pc  $\alpha$ -phase and Zn–Pc amorphous) a new Lorentzian band with maximum at 1.4 eV and half-width of 0.7 eV. This band is assigned to a new low energy CT transition derived from the interaction between Zn–Pc and C<sub>60</sub>. Additional spectroscopic investigations confirm this assignment (*vide infra*).

## B. Photoluminescence

We have compared the photoluminescence spectra (PL) performed, in the same experimental conditions, of two films deposited on quartz substrates of Zn–Pc and C<sub>60</sub> of equivalent thickness and composition but with different structures. One film was obtained by depositing two layers of 25 nm of C<sub>60</sub> and 25 nm of Zn–Pc (double-layer) while the second film (50 nm) was obtained by co-sublimation of the two molecules (50%, 50%) (co-sublimated). The PL spectra of the two films obtained exciting at 2.54 eV in air at room

temperature are reported in Fig 4. The spectrum of the double layer shows a low energy tail that vanishes at about 0.75 eV with superimposed a relatively narrow peak at 0.97 eV (see Fig.4, dotted line). The PL tail is the sum of two contributions from C<sub>60</sub> emission (mainly from deep traps <sup>29-30</sup>) and Zn–Pc phosphorescence <sup>31-37</sup>. The peak at 0.97 eV, observed only in the sample exposed to air, is assigned to the emission from singlet oxygen O<sub>2</sub> (Ref 29) that is populated, via energy transfer, from the photoinduced C<sub>60</sub> triplet state. Despite the very short lifetime of the triplet excitations in the aggregated state of C<sub>60</sub> (<20 ps <sup>38</sup>) the energy transfer from C<sub>60</sub> triplet to oxygen singlet is so efficient that the presence of a small oxygen contamination can be revealed by the observation of the singlet oxygen PL.

The PL spectrum of the cosublimated film is completely different from the one obtained from the double layer. The PL intensity is suppressed by several orders of magnitude and is red-shifted with a maximum at 0.95 eV (FWHM = 0.5 eV). The PL contributions of the single components of C<sub>60</sub> and Zn–Pc disappear completely as well as the singlet oxygen emission at 0.97 eV. The shape of the new PL is the mirror image of the new absorption band at 1.4 eV observed in the same film (see Fig.5). The presence of this new band and the suppression of the emission both from C<sub>60</sub> and Zn–Pc indicate the existence of a new excited electronic level, at lower energy, that efficiently collects and relaxes nonradiatively the excitons.

### C. Photoconductivity

We have investigated the response in the near infrared of different *p–n* junctions built using C<sub>60</sub> as *n*-type and Zn–Pc as *p*-type component that acts as a photovoltaic (PV) cell. In particular, we have compared two junctions with a different interface among the *p* and *n* materials that, for simplicity, we will refer to as flat and rough interfaces. The flat interface device consists of a double layer structure of the two compounds subsequently sublimated on transparent ITO with an aluminum counterelectrode [ITO/Zn–Pc/C<sub>60</sub>/Al]; the latter device (rough interface) is prepared by depositing an intermediate layer of 30 nm by co-sublimation of the two molecules [ITO/Zn–Pc/(Zn–Pc + C<sub>60</sub>)/C<sub>60</sub>/Al] (see Fig.6). As already mentioned, the structure of the co-sublimated layer is characterized by a spinodal decomposition where the two materials tends to segregate forming microdomains of a single component where the other molecule is present only in a very diluted concentration

acting as dopant (Zn–Pc for C<sub>60</sub> and vice versa). In the case of the PV device the structure derived from the spinodal decomposition can be envisaged as an interdigitated (interpenetrated) *p–n* junction with a very large interface surface (rough interface) extending in three dimensions<sup>15</sup> In both devices, the action spectrum reveals a photocurrent response by exciting in the NIR. Though in the case of flat interface it is more than an order of magnitude smaller than for the interdigitated one. Differences among the photocurrent responses of the two PV cells are concerning not only the efficiency but also the dynamics of the photocarriers. In fact, the intensity dependence of the photocurrent by exciting at 1.16 eV is different for the two devices. In Fig.7, the short circuit current  $I_{sc}$  exciting at 1.16 eV is reported for both the flat and the rough interface devices. The flat interface device shows square root dependence with laser intensity  $I_{Las}$  ( $I_{sc} \propto I_{Las}^{0.49}$ ; Fig 7, open squares). On the other hand, the rough interface device (Fig.7, solid triangles) shows linear power dependence of the photocurrent.

#### D. Raman

The charge state and or the environment of molecules can effect the energy of vibrational modes of molecules. In the case of C<sub>60</sub>, the Raman active *A<sub>g</sub>(2)* "pinch" mode shows a large and linear shift of about 6–7 cm<sup>-1</sup> per electron accommodated on the molecule independently on the kind of dopant [alkali metal<sup>39-40</sup> or organic molecule like TDAE<sup>41</sup>]. On the contrary no significant change in energy for this tangential mode has been observed as a consequence of the crystal field or of the interaction with solvents (the larger shift observed was 1 cm<sup>-1</sup> in CS<sub>2</sub> solution<sup>42</sup>). Consequently, the observation of a shift of the *A<sub>g</sub>(2)* is a good monitor of the amount of extra charge accommodated onto a single C<sub>60</sub> molecule. We have performed Raman scattering characterization in the co-sublimated film using different excitation energies.

The Raman spectrum of the co-sublimated film obtained by exciting in the visible ( $E_{ex}$  = 1.96, 2.41 and 2.54 eV) does not exhibit any relevant change in the spectral features with respect to the sum of those of the two C<sub>60</sub> and Zn–Pc components. On the other hand, when the Raman scattering of the co-sublimated Zn–Pc/C<sub>60</sub> film is measured by exciting in the NIR, at 1.16 eV, (i.e., close to the new band observed in absorption), a change in the peak position and shape of the *A<sub>g</sub>(2)* pinch mode with respect to the pristine C<sub>60</sub> is clearly observed. While it is possible to fit the *A<sub>g</sub>(2)* peak of the single component C<sub>60</sub> film only by using a single Gaussian–Lorentzian peak [Fig. 8 (a) dashed line], it is necessary to

introduce a second component to fit the spectrum of the co-sublimated film. The best fit is obtained by adding to the Gaussian–Lorentzian band used to fit the spectrum of the pristine C<sub>60</sub> film [Fig. 8 (b), dashed line] a second band 15% broader and red-shifted by 1.8 cm<sup>-1</sup> with respect to the former peak [Fig. 8 (b), dotted line].

## IV. DISCUSSION

All the experimental results obtained with a large variety of techniques show and characterize the existence of a weak CT ground state that is induced by the interaction between Zn–Pc and C<sub>60</sub>.

The PL spectrum with maximum at 0.97 eV as well as the new absorption peak at 1.4 eV, observed in the co-sublimated films (see Fig 5), define the location of the new electronic CT transition associated to the complex formed by the two molecules. The relative weight of the different components strongly depends on the growth condition of the film. At this concentration (Zn–Pc 50% and C<sub>60</sub> 50%), it is almost impossible to avoid the occurrence of a spinodal decomposition of the blend with segregation in grains (of larger or smaller sizes) of the single components that, in the case of Zn–Pc, are in the  $\alpha$ -phase. Consequently, by considering that the  $\alpha$ -phase can be associated with the bulk (volume) of grains, while the amorphous is the fingerprint of the Zn–Pc molecules either at the grain surface or dispersed in the C<sub>60</sub> clusters, it is possible to obtain a rough estimate of the average domain dimension. The ratio of  $\alpha$  and amorphous phase that can be derived from the absorption spectra coincides with the volume/surface ratio (normalized using the van der Waals dimensions of the single molecule) that, for a sphere of radius  $r$ , corresponds to  $r/3$ . Using this approximation we estimate that the nonbulk Zn–Pc is about the 15% of the total amount of the donor material and consequently that the Zn–Pc grain diameter is of the order of 10–20 nm.

The complete bleaching of the PL of C<sub>60</sub> and Zn–Pc indicates that the dimension of grains of the different phases derived from the spinodal decomposition is smaller than the diffusion length of the photogenerated excitons. Considering that the estimated mean free path for excitons in M–Pc from organic photovoltaic device is of the order of magnitude of 20–30 nm<sup>12</sup> the total suppression of PL contributions from the nonperturbed components indicates that either the dimension of the domains or that the mean distance of the few heteromolecules dissolved within this nanostructures is smaller than the exciton mean free path.



As already mentioned, the efficiency of excitation transfer among triplet  $C_{60}$  and oxygen singlet is very high, despite the short lifetime of the triplet in the solid state. The absence of the oxygen singlet emission peak in the PL spectrum of the co-sublimated film in air reveals that in this system also the triplet formation in  $C_{60}$  is inhibited as a consequence of the formation of a CT ground state. This is quite important for any application of the system in optical devices exposed to both oxygen and light. In fact, it has been shown<sup>43</sup> that singlet oxygen is the responsible of photodegradation of  $C_{60}$  inducing oxygen incision of the carbon cage. The electronically excited molecular oxygen can react with  $C_{60}$  severing a C = C bond and forming two C = O carbonyl groups per oxygen molecule.

Photoconductivity measurements in M-Pc system have shown a sub-linear response with the power intensity at photon energy of the order 1.1 eV<sup>44</sup> Such a response can be ascribed to the very weak absorption in this spectral range associated to spin-forbidden singlet-triplet transition that became partially allowed because of the spin-orbit coupling due to the heavy atom. The observed photo-carriers are generated by triplet-triplet

annihilation and consequently the power dependence is sublinear ( $\propto I^{1/2}$ ) been determined by the combined probability of two independent events. The flat interface device shows a weak short circuit current with almost square root dependence with the excitation intensity at 1.16 eV. This clearly indicates that, in this case, most of the photogenerated carriers derive from a two body recombination mechanism, like triplet-triplet annihilation in Zn-Pc close to the interface with  $C_{60}$  behaving as in the case of a M-Pc Schottky structure<sup>44</sup> The large increase of the efficiency of the rough interface junction with respect to the flat one, indicates that most of the carriers are generated in the intermediate co-sublimated layer by a much more efficient process than via triplet bimolecular recombination. The linear power dependence of the photocurrent indicates that the carrier formation is a one-photon process. This excludes that charge carriers are generated in the co-sublimated region by triplet-triplet annihilation, because it would show square root dependence. Moreover, the linear behavior of the photocurrent versus light intensity at 1.16 eV rules out any possible interpretation of the experimental features in this spectral region, the absorption tail, and the photoluminescence peak, as absorption or emission from in-gap localized states due to disorder. In fact, as in the case of triplet-triplet annihilation, also in this case the photogeneration mechanisms would be a two body event. The energy of the photons (1.16 eV) falls in the absorption band associated with the CT. Once the Zn-Pc/ $C_{60}$  complex is excited (photon + CT  $\rightarrow$  CT\*) it can evolve either returning

to the ground state by nonradiative/radiative recombination or it can give rise to charge separation producing fully ionic molecules ( $CT^* \rightarrow |A^- \rangle + |D^+ \rangle$ ). This process is schematically represented in Fig. 9. Together with the energy levels derived from the absorption measurements described in Sec. III A, the energy values reported in the figure are also consistent with those obtained from UPS data for different  $C_{60}/M-Pc$  composites

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The Raman spectra of the co-sublimated film (see Sec. III D) by exciting at 1.16 eV show two peaks in the  $A_g(2)$  energy range. As already discussed, because of the spinodal decomposition, the sample is not single phase and the observation of two peaks associated with the same mode can be attributed to the presence of two types of  $C_{60}$  molecules: one that is unperturbed (undoped) and a second that is partly doped. This confirms what was observed in the NIR-VIS-UV absorption spectra. The occurrence of the spinodal decomposition account for two types of  $C_{60}$  molecules, the unperturbed in the interior of the  $C_{60}$  aggregates, and the perturbed one at the interface between  $C_{60}$  and Zn-Pc aggregates. Only the latter  $C_{60}$  molecules are contributing to the formation of a CT state. From the red shift of the second component of the  $A_g(2)$  mode it is possible to estimate the amount of charge transferred in the ground state to the  $C_{60}$  from the Zn-Pc. In the linear approximation, the softening of  $1.8 \text{ cm}^{-1}$  measured for the second spectral component in the co-sublimated film corresponds to a net transfer of approximately  $0.25 e^-$ . These results are consistent with a ground state CT of about one-fourth of an electron to the  $C_{60}$  molecule which causes a weak absorption cross section with maximum at 1.4 eV. The resonant nature of the Raman scattering can explain why the second component for the  $A_g(2)$  pinch mode is observed only by exciting at 1.16 eV and not by using visible excitation. In fact, the photons at 1.16 eV are in near resonance with the CT transition at 1.4 eV. Consequently, the presence of a minor component of partially "doped"  $C_{60}$  can be resonantly enhanced with respect to the rest of the undoped  $C_{60}$ , becoming strong enough to be detected. As a consequence, because of its resonant nature, the Raman scattering, in this case, cannot be considered as a quantitative measurement of the amount of a particular component; hence, the ratio of the two components of the  $A_g(2)$  mode observed exciting at 1.16 eV cannot be used to measure directly the ratio of neutral and partially doped  $C_{60}$ .

## V. CONCLUSIONS

In this paper, we have shown for the first time that, in the condensed phase,  $C_{60}$  and Zn-Pc adjacent molecules form a complex whose ground state has a weak CT character. Such a complex can be interpreted in terms of  $A-D$  moieties, forming a weakly ionic pair. The detailed and various information collected using different experimental techniques, allows us to describe satisfactorily the CT state. This new state, with maximum absorption at 1.4 eV, shows a net electron transfer from Zn-Pc to  $C_{60}$  of approximately  $0.25 e^-$ . The CT state provides an efficient nonradiative decay pathway, which eventually evolves in long-lived separate carriers, quenching the photoluminescence of both Zn-Pc and  $C_{60}$ .

In Sec. III C, we have already shown that it is possible to develop a heterojunction type organic photovoltaic cell by using  $C_{60}$  and Zn-Pc as  $n$  and  $p$ -type components respectively. In this case, an intermediate co-sublimated  $C_{60}/\text{Zn-Pc}$  layer improves significantly the efficiency of the system<sup>15</sup> Such an improvement is only partially related to the direct photogeneration of free carriers in the NIR. The occurrence in the co-sublimated region of spinodal decomposition is providing a complex structure of the interface that following a percolation of the grains of the different components is extending in three dimensions the surface of the  $p-n$  junction increasing the active volume of the device.

As it was described in a recent paper such a system can be used also as a new route to develop optical limiting reverse saturable absorption in the NIR that take advantage of the overlapping in energy of the weak CT ground state absorption and the larger cross section of the LUMO-LUMO + 1 transition of the  $C_{60}$  ion<sup>45</sup> The efficiency of the device, in this case, is limited by the spinodal decomposition that reduces the amount of molecules in the film taking part in the process. A detailed study of the domain size and optical properties of films of Zn-Pc and  $C_{60}$  at various concentrations versus growth conditions is now in progress.

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## FIGURES

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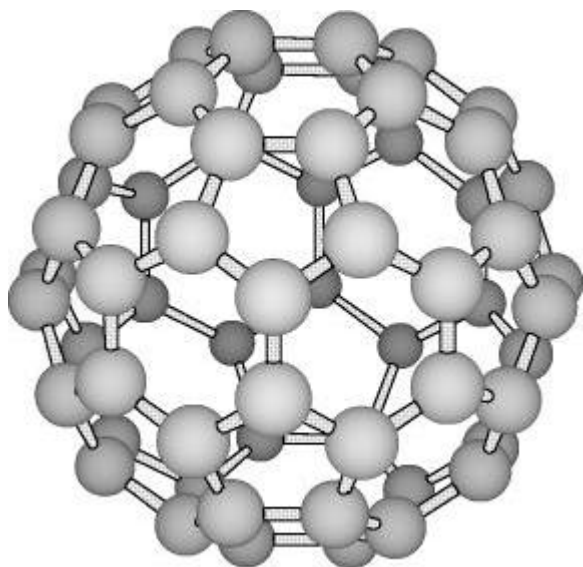


Fig. 1. The fullerene C<sub>60</sub> molecule.

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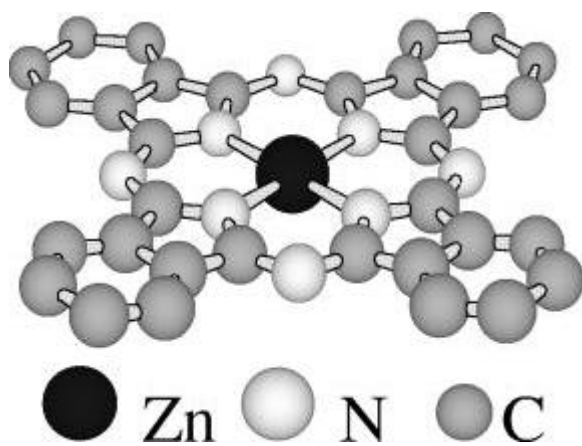


Fig. 2. The Zn-phthalocyanine molecule.

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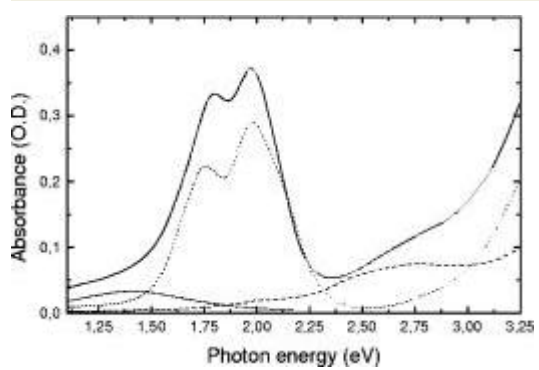


Fig. 3. Absorption spectra films on quartz of a 30 nm thick film of  $C_{60}$  (dashed line), a 30 nm thick film of Zn-Pc (dotted line), and a 60 nm thick film of co-sublimated Zn-Pc/ $C_{60}$  (solid line). The dashed-dotted line represents the absorption peak derived from analysis of the absorption spectrum of a co-sublimated film of Zn-Pc and  $C_{60}$ .

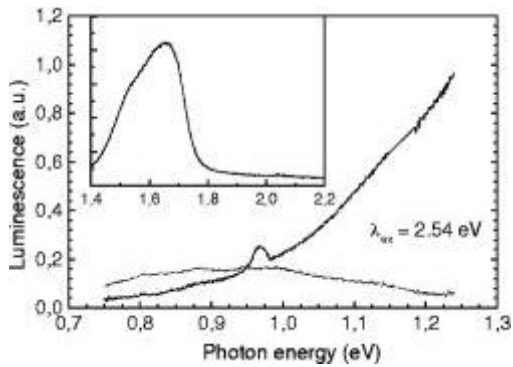


Fig. 4. Near-infrared photoluminescence spectra of the double layer film of Zn-Pc (25 nm) and  $C_{60}$  (25 nm) (solid line) and of a 50 nm co-sublimated film of Zn-Pc and  $C_{60}$  (dotted line). The inset shows the PL spectrum of the double layer film in the 1.4–2.2 eV range.

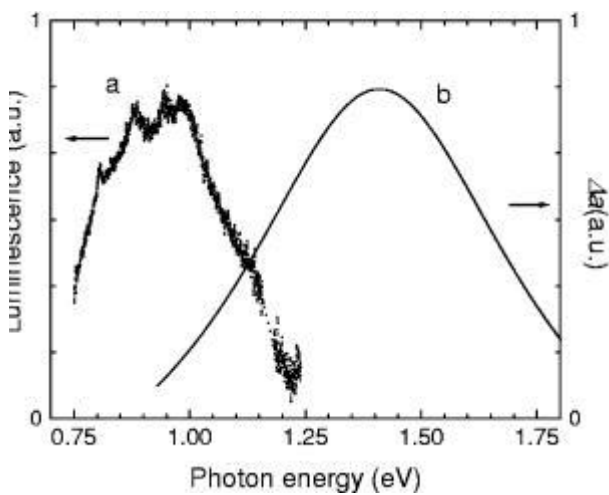


Fig. 5. (a) Photoluminescence of a co-sublimated film of Zn-Pc and  $C_{60}$ ; (b) absorption peak derived from analysis of the absorption spectrum of a co-sublimated film of Zn-Pc and  $C_{60}$ .

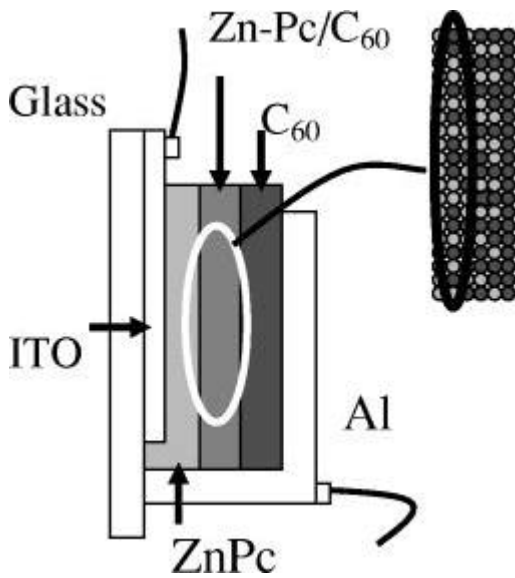


Fig. 6. A schematic representation of the  $p$ - $n$  junction cell built depositing on a transparent ITO electrode a multilayer structure of Zn-Pc and C<sub>60</sub> interposing a 30 nm co-sublimated ZnPc/C<sub>60</sub> layer.

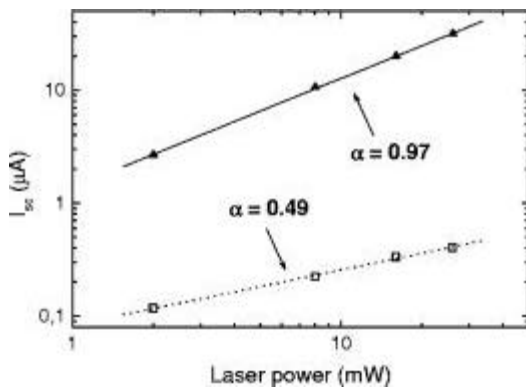


Fig. 7. Log-log power dependence of the short circuit current ( $I_{sc}$ ) of two photovoltaic  $p$ - $n$  junction cells. The two cells have a common structure: glass-ITO/Zn-Pc( $p$ )/C<sub>60</sub>( $n$ )/Al. One of the two cell (▲) has been grown separating the two single component layers Zn-Pc ( $n$ ) and C<sub>60</sub> ( $p$ ) with a 30 nm co-sublimated Zn-Pc/C<sub>60</sub> layer: glass-ITO/Zn-Pc( $p$ )/(Zn-Pc + C<sub>60</sub>)/C<sub>60</sub>( $n$ )/Al; lines are fittings of the experimental data using the power function  $I_{sc} \propto I_{LA}^{\alpha}$ .



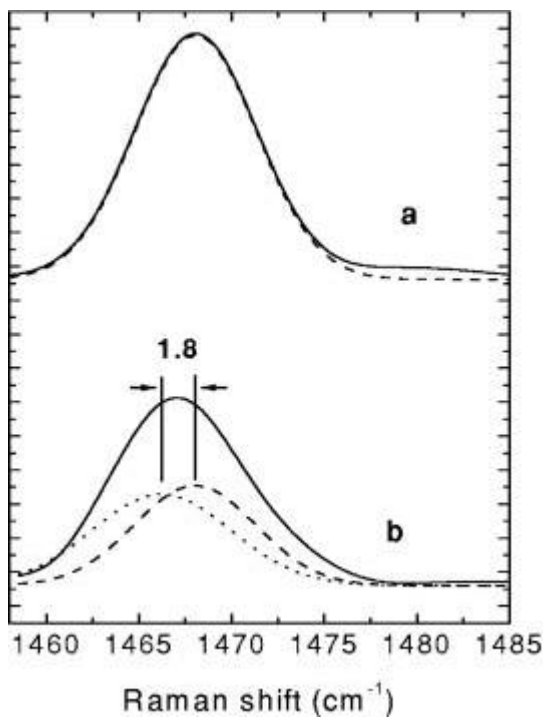


Fig. 8. (a) The Raman spectrum of a single component C<sub>60</sub> film (solid line) and the fitting peak (dashed line); (b) The Raman spectrum of a co-sublimated Zn-Pc/C<sub>60</sub> film (solid line) and the two fitting peaks (dashed and dotted lines).

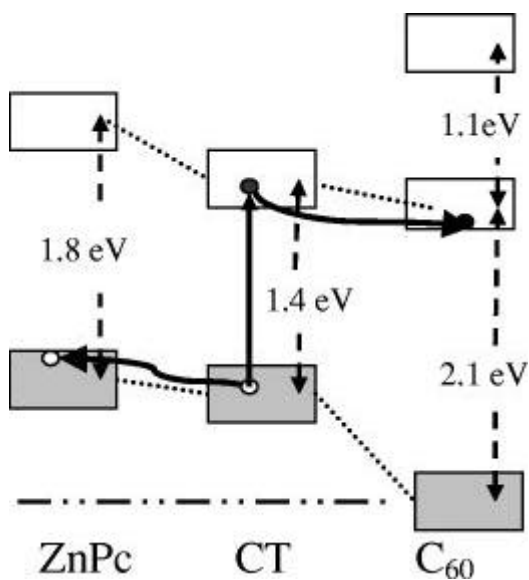


Fig. 9. Energy level scheme of the CT state with respect to the Zn-Pc and C<sub>60</sub>. Continuous line arrows represent photoexcitation and the possible decay path in separate charges.