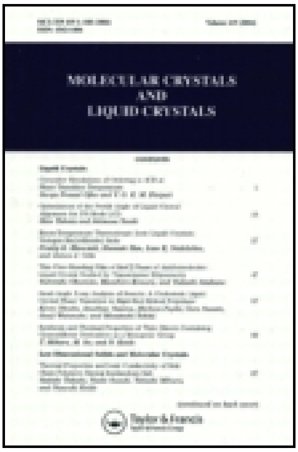

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Spectral Characteristics of C_{60}-Conducting Polymer Junctions: Various Molecular D-A Type Photocells

S. Morita [a], S. B. Lee [b], A. A. Zakhidov [b] & K. Yoshino [a]

[a] Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, 565, Japan

[b] Department of Thermophysics, Uzbek Academy of Sciences, Katartal 28 Chilanzar C, Tashkent, 700135, Uzbekistan

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SPECTRAL CHARACTERISTICS OF C60-CONDUCTING POLYMER JUNCTIONS: VARIOUS MOLECULAR D-A TYPE PHOTOCELLS.

S. MORITA , S.B. LEE*, A.A. ZAKHIDOV* AND K. YOSHINO
Department of Electronic Engineering, Faculty of Engineering, Osaka University,
2-1 Yamada-Oka, Suita, Osaka 565, Japan
* Department of Thermophysics, Uzbek Academy of Sciences,
Katartal 28 Chilanzar C, Tashkent, 700135, Uzbekistan

Abstract We have found recently that thin film layered heterojunction between C_{60} and conducting polymer, like poly(3-alkylthiophene) (PAT) shows a photovoltaic effect due to photoinduced charge transfer at the interface. Here we describe two other examples of such photocells in RO-PPV/C_{60} and PPP/C_{60} heterojunctions and study their spectral characteristics. Contrary to conventional inorganic semiconductor p-n junction photocells, the C_{60}-PAT junction can be rather viewed as molecular donor-acceptor (D-A) type photocell in which the processes of photogeneration and separation of charge carriers are quite distinct. In a p-n junction free electron-hole pairs are known to be primarily photogenerated at interband transition and then separated in the internal electric field of the barrier, while in D-A molecular photocell mainly neutral excitons are first created by light, with charges being primarily separated at the narrow interface region due to D-A type intermolecular charge transfer interactions. We analyze how this processes depend on the wavelength of the pumping light and on the polarity and magnitude of the applied voltage.

INTRODUCTION

We have proposed recently to intercalate C_{60} into conducting polymers, and to form heterojunction between them.[1-7] In such cases, quenching of photoluminescence and enhancement of photoconductivity have been also observed.[1,3-5] These indicate that, photoinduced charge transfer occurs between the conducting polymer and C_{60}, as suggested by us.[1,3,4] We have also suggested that the photoinduced charge transfer effect can be applied to various uses such as in photoconductors, photovoltaic cells and electrophotography.[5] Recently, Sariciftci et al. also reported effects of photoinduced charge transfer between C_{60} and poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene).[8]

In the present paper various types of heterojunctions are studied:The poly(3-alkylthiophene)/ C_{60}, OO-PPV/C_{60} and PPP/C_{60} junctions are prepared and the effect of light irradiation, especially the wavelength dependence of its junction characteristics, is studied.

EXPERIMENTAL

Poly(3-alkylthiophene) was obtained from the corresponding monomer utilizing $FeCl_3$ as a catalyst. Details of the preparation and purification method and procedure were already reported in our previous paper.[9] Among various forms of poly(3-alkylthiophene), poly(3-octadecylthiophene) with alkyl chain length n=18 was used in this experiment. C_{60}, prepared by arc discharge from graphite and washing with toluene, and provided by Science Laboratories Co.,

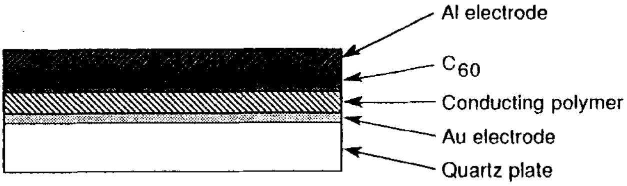

FIGURE 1 Layer structure of poly(3-alkylthiophene)/C_{60} junction.

Ltd., was used.

The poly(3-alkylthiophene)/C_{60} junction consists of a transparent gold electrode deposited on a quartz plate, a poly(3-alkylthiophene) layer, a C_{60} deposited layer and an aluminum electrode, as shown in Fig.1. The poly(3-alkylthiophene) layer was cast from chloroform solution onto the substrate. The C_{60} layer was vacuum-deposited onto the poly(3-alkylthiophene)-coated substrate. Aluminum was vacuum-deposited on top of the device as a second electrode. OO-PPV/C_{60} junction was prepared in a similar way.

We have used the powder of PPP prepared according to the method of Kovacic. The Al/C_{60}/PPP/SnO_2 heterostructure have been prepared according the following procedure. The thin film of PPP were obtained by discrete vacuum evaporation of PPP-powder onto a glass slides with the tin-oxide conducting transparent coating. Evaporation of C_{60} onto the PPP thin film was performed by heating the C_{60} powder in a Mo crucible at 600°C. Then the procedure was ended by vacuum evaporation the front semi-transparent Al electrode onto the obtained C_{60}/PPP heterostructure.

FULLERENE / POLYALKYLTHIOPHENE PHOTOCELL

Figure 2 shows photoresponse spectra of the device. Xe arc lamp light passing through a monochromator was irradiated from a quartz plate. The term "negative bias" means that negative voltage is applied to the gold electrode. In the case of the applied voltage of -1V, a large photoresponse was observed, as evident in Fig.2. Two photoresponse peaks were observed at

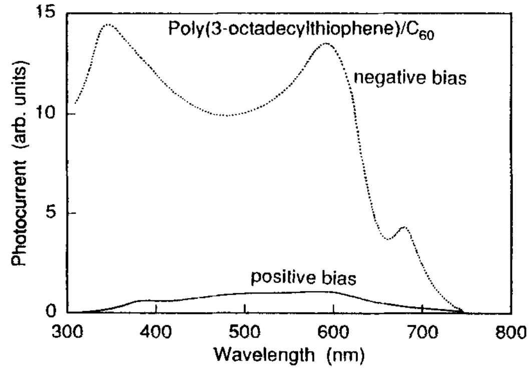

FIGURE 2 Photoresponse of poly(3-alkylthiophene)/C_{60} junction.

about 350 nm and 580 nm, which correspond to the h_u-t_{1g} transition of C_{60} and π-π* transition of poly(3-octadecylthiophene), respectively. Each transition was observed in absorption spectra of C_{60} and poly(3-octadecylthiophene).[5,6] Moreover, the small photoresponse was observed at 680nm, as evident in this figure. This transition is considered to be due to the h_u-t_{1u} transition of C_{60} which is the forbidden transition and was not observed in the absorption spectrum of C_{60} in solution. However it was theoretically indicated that this dipole forbidden transition of a single C_{60} molecule become dipole-allowed in some extent by lattice-fluctuation or intermolecular interactions[10] and this transition was clearly observed in the photoconduction spectra of C_{60}/C_{70} film[11] and C_{60}-conducting polymer composite.[12] On the other hand, in the case of positive bias, the photoresponse was very small compared with the case of negative bias. These results can be interpreted as follows.

We have shown the photoinduced charge transfer between conducting polymer and C_{60} so far.[1,3-5] That is, an electron photoexcited by π-π* transition in the conducting polymer can be transferred to C_{60}, and a hole, photogenerated by h_u-t_{1g} and h_u-t_{1u} transitions in C_{60}, injected to the conducting polymer. These charge transfer directions are in agreement with the negative bias direction in this case. Therefore, by applying negative bias, the photoinduced charge transfer is activated and accelerated, resulting in the large photoresponse. The fact that the photovoltaic signal was induced significantly by light corresponding to the h_u-t_{1u} forbidden transition in C_{60}, even at negligible absorption, can tentatively be interpreted as follows. In spite of the small probability of excitation to the t_{1u} state, due to the forbidden transition, the excited state should have longer lifetime than that of the allowed excitation, resulting in the higher probability of hole transition from C_{60} to poly(3-alkylthiophene).

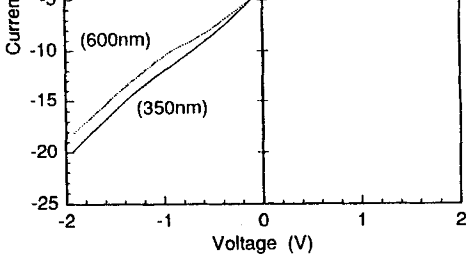

FIGURE 3 Current-voltage characteristics of poly(3-octadecylthiophene)/C_{60} junction under light irradiation and dark conditions.

On the other hand, in the case of positive (+ on Au) bias, the photoinduced charge transfer is not enhanced because the electric field direction is inverse to the charge transfer direction from poly(3-alkylthiophene) to C_{60}, resulting in the small photoresponse. Recently, Sariciftci et al. also detected photoinduced voltage in the poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene)/C_{60} system.[13]

Figure 3 shows current-voltage characteristics of the poly(3-octadecylthiophene)/C_{60} junction under light illumination and dark conditions. As evident in this figure, the photovoltaic effect was observed due to the photoinduced charge transfer. With irradiation of light of 350 nm in wavelength, with which the photoresponse peak of C_{60} was observed, the current was enhanced with negative bias voltage but saturated with positive bias. These are opposite characteristics to

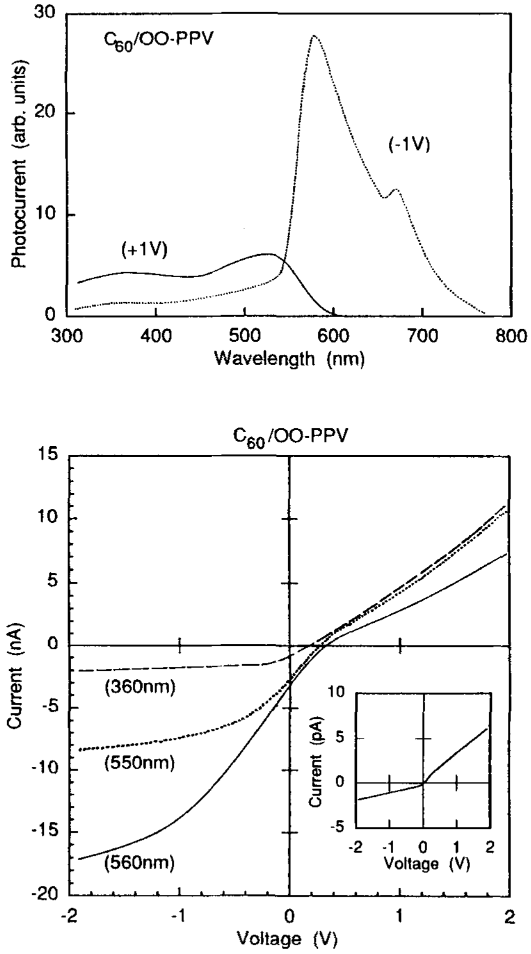

FIGURE 4 (a) Photoresponse of Al/C_{60}/OO-PPV/Au heterostructure and (b) dependence of current on voltage of Al/C_{60}/OO-PPV/Au heterostructure in various irradiation wavelength. (inset shows dark I-V characteristics) those under dark conditions. Under irradiation of light of 600 nm, with which the photoresponse of poly(3-octadecylthiophene) was observed, the current with the negative bias was enhanced just as in the case of 350 nm light irradiation, and with the positive bias it was also slightly enhanced, contrary to the case of 350 nm light irradiation. These results indicate that the current-voltage characteristics under light illumination depend on the light wavelength. The reason for this wavelength dependence is discussed in next section.

FULLERENE/OO-PPV and FULLERENE/PPP PHOTOCELL

Let now turn to C_{60}/conjugated polymer heterojunctions, which also like PAT/C_{60} above resembles the model of molecular type Donor-Acceptor diode of Aviram and Ratner.[14] In the Al/C_{60}/conducting polymer/Au layer structure, photo response was observed upon light irradiation as shown in Fig.4 a). In this case, it should be noted (in this figure RO-PPV with octyl side chain was used as a conducting polymer) large polarity effect was also observed. The sample was irradiated by monochromated light from the side of semi-transparent Au electrode deposited on glass.

In the case of forward bias (that is, Au electrode is positively biased as above) larger dark current has been observed than in the backward bias (Au is negative) in consistency with D-A rectification,[14] since OO-PPV is a donor and C_{60} is an acceptor in this D-A rectifier, as sketched in Fig.5. The original idea of Aviram and Ratner[14] was to inject electrons to LUMO of A molecule at forward bias from low work function electrode (Al in our case), and to inject holes to HOMO of

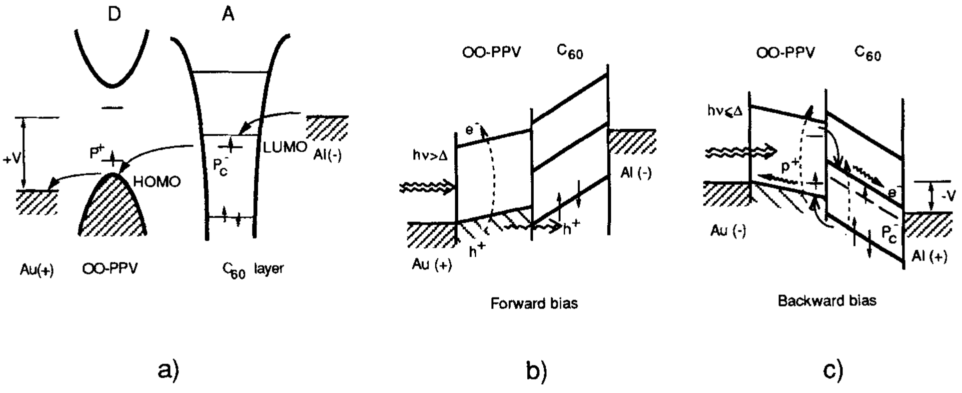

FIGURE 5 Schematic illustration of electron transfer between fullerene and conducting polymers (a)rectification in D-A molecular layer diode at forward bias V>0, under dark conditions, (b)photogeneration of e^--h^+ paire at the electrode region; photo-induced charge transfer at interface is not important although hole tunneling, shown by wa vy arrow is possible, (c)photo-induced charge transfer at C_{60}/OO-PPV interface (shown by solid arrows) contributes to enhanced photoresponse at hν>Δ.

D from hole injecting contact (Au in our case), so that recombination of e^- and h^+ at interface will complete the forward dark current as sketched at Fig.5. Clearly at backward bias such process needs much higher voltage for the transmission of current, providing rectification as observed in our case, with the only difference that charges are not free e^- and h^+ on molecular levels, but rather P^+ and Pc^- on the corresponding local levels of polarons. Same D-A layer upon light irradiation provides photoinduced charge separation at the interface due to favorable e^- transfer from LUMO of D (or exciton(Ex) level of OO-PPV in our case) to LUMO of A (to t_{1u} level of C_{60}) or hole transfer from h_u level of C_{60} to valence band of polymer, followed by self trapping to corresponding polaronic states, providing photovoltage (at open circuit) or photocurrent (if short circuited).

Upon photoexcitation indeed at the backward bias large signal was observed in the range of photon energy near the band gap. In the spectrum, photoresponse was also found at around 680 nm which corresponds to the transition from h_u to t_{1u} in C_{60}. However, much smaller signal was observed at the wavelength larger than the band gap of OO-PPV and the response at higher photon energy was negligible.

On the other hand in the case of positive polarity (Au is positively biased) photoresponse was only observed at photon energy larger than the band gap energy as shown at Fig.4. The corresponding open circuit voltage Uoc= 0.2 eV at 560-580 nm excitation, while the short circuit current Isc = 3 nA is comparatively small due to large serial resistance of the thick enough layer of semiconducting C_{60}.

It should also be noted in Fig.4,b) that the current-voltage characteristics of this layered structure element was strongly dependent on the wavelength of the excitation. That is, for the photon energy much larger than the band gap energy of OO-PPV, the photoresponse for the backward bias saturates with increasing voltage. On the other hand, that at photon energies around the band gap photocurrent increased more with voltage.

These results on Al/C_{60}/OO-PPV/Au layer can be explained as follows. In the case of backward bias, the response should be due to the photoinduced charge transfer between OO-PPV and C_{60} crossing the junction as sketched at Fig.5,c). Photoseparated P^+ in OO-PPV and Pc^- in C_{60} layers drift down the potential and are collected at electrodes. Note that electric field drop is mainly in C_{60} layer due to its higher resistivity. This behaviour is quite similar to the photocurrent enhancement in the conventional p/n type photodiode at the reversed bias. However the light with energy much larger than the band gap of OO-PPV does not reach the junction area due to large absorption in the bulk of OO-PPV. Therefore the response is mainly observed in the region around the band gap energy, where Ex excited at the interface can dissociate into P^+ and Pc^- due to intermolecular charge transfer. At 680 nm the h_u-t_{1u} transition in C_{60} layer is also possible followed by h^+ transfer to OO-PPV layer (Fig.5,c)), which gives a small peak in photoresponse at backward bias of Fig.4a). On the other hand, in the case of positive bias the carriers excited near the Au electrode by light of photon energy larger than the band gap can contribute to the photoresponse, since P^- from OO-PPV will be drifted to Au, while P^+ may drift up the electric field and can be collected at Al electrode if have chance to cross the interface due to thermal excitation or tunneling across the barrier between OO-PPV and C_{60}, shown at Fig.5,b) bywa vy arrow. In this case also the light with the energy around the band gap can reach the junction area and create photoseparated carriers. However, because the polarity of Al is positive, the electron even if have been transferred to C_{60}, can not be collected at Al electrode (and hole in P^+ separated at interface can not be collected at Au electrode), and thus not contributing to photocurrent, resulting thus in the negligible response for positive bias.

The saturation in current voltage characteristics observed for backward bias can be interpreted as follows. The excited carrier density at around junction interface by light with photon energy much larger than the band gap is very low because such light is attenuated strongly by the absorption of the bulk of OO-PPV. In such a case, the saturation effect can occur as observed in the experiment due to the limited concentration of excitons (or P^- in OO-PPV) to provide the electron for the transfer from OO-PPV to C_{60}. That is in this case the photoexcitations generation is rate determining factor for the photoresponse. Therefore, with increasing light intensity, the number of carriers separated across the interface also increases and the saturation field in the current-voltage characteristics, needed to collect all this carriers should shift to higher voltage.

So the effect of the photoinduced charge transfer between OO-PPV and C_{60} takes place only at the interface region, due to dissociation of neutral photoexcitations both in C_{60} and OO-PPV, which can be also influenced by electric field. This photoinduced charge transfer contributes to photocurrent only upon backward bias (and give sizable photovoltaic effect with Uoc = 0.2 eV at open circuit), while the carriers generated at the electrode regions give rise of photocurrent at forward bias.

The I-V characteristics of $Al/C_{60}/PPP/SnO_2$ heterostructure in the dark and under UV-illumination were measured at room temperature. The heterostructure have showed the asymmetric dark I-V dependence with rectification ration about 10^4 at 20V. Upon illumination the two-orders of magnitude increase of current was observed at -20 V of reverse bias (Au electrode as negative electrode) and the three orders of magnitude rise of current at increasing reverse bias in the full range from 0 V to 20 V. Detailed study on characteristics of $Al/C_{60}/PPP/SnO_2$ are now under progress.

In conclusion, we prepared poly(3-alkylthiophene)/C_{60}, RO-PPV/C_{60} and PPP/C_{60} junction devices. The observed photovoltaic response gave evidence of the photoinduced charge transfer between all conducting polymers and C_{60}. The effect of the photoinduced charge transfer also influenced the current-voltage characteristics. The current-voltage characteristics were found to depend on the wavelength of the illumination light. These results can be explained in terms of photoexcited electron transfer from polymer layer to C_{60} layer, and photoexcited hole transfer from C_{60} to the polymeric chains at the interface of PPP/C_{60} junction, which is viewed as molecular photocell,[14] similar to vectorial photoseparation in D-A interchain heterojunction.[15]

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