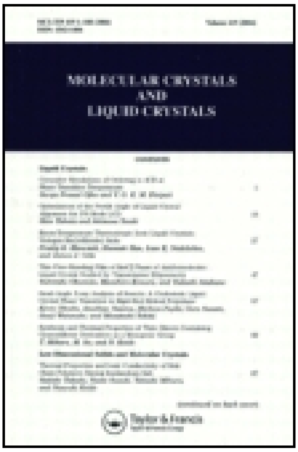

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Optical Properties of Fullerene Doped Conducting Polymers: Scenario of Photo Process, Persistent Photoconductivity and Enhanced Electroluminescence Quenching

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To cite this article: Katsumi Yoshino , Tatsuo Akashi , Kenji Yoshimoto , Masayoshi Yoshida , Shigenori Morita & Anvar A. Zakhidov (1994): Novel Optical Properties of Fullerene Doped Conducting Polymers: Scenario of Photo Process, Persistent Photoconductivity and Enhanced Electroluminescence Quenching, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 343-357

To link to this article: http://dx.doi.org/10.1080/10587259408039265

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 343–357
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NOVEL OPTICAL PROPERTIES OF FULLERENE DOPED CONDUCTING POLYMERS:

Scenario of Photo Process, Persistent Photoconductivity and Enhanced Electroluminescence Quenching

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Abstract Earlier we found that photoluminescence (PL) in conducting polymer with non-degenerated ground state (NDGS CP) is quenched remarkably upon doping by small amount of fullerenes such as C_{60} and C_{70}. Here we show that electroluminescence is quenched even much more stronger indicating that each C_{60} molecule acts as a multiple trapping and/or recombination center for carriers. On the other hand photoconductivity (PC) in NDGS CP and also in conducting polymer with degenerated ground state (DGS CP) such as polyacetylene derivatives is enhanced significantly upon fullerene doping at the excitation of (a) the wavelengths of the inter-band transition in conducting polymer and (b) allowed and (c) forbidden optical transitions in fullerene. Remarkable polarity effect is observed in the spectral response of enhanced photoconductivity, proving that positively charged mobile carriers in polymeric chains contribute to PC.

The effect of persistent photoconductivity at room temperature is found in C_{60}/CP (conducting polymer) nanocomposites and we present first results on its dependence on C_{60} concentration, light intensity and temperature.

These unique characteristics are discussed in frames of the general scenario of photogeneration enhancement in NDGS and DGS polymers due to photo-induced (or injection controlled) charge transfer between conducting polymers and fullerenes, emphasizing the role of self-trapped excitations: exciton-polarons, polarons and charged solitons in polymer main chain and string type polarons and bipolarons in C_{60} spherical molecules. It is suggested that bipolarons of C_{60}, BP_c^{2-}, play important role in persistent photoconductivity and EL quenching due to their long lifetime.

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1. INTRODUCTION

Recently we have proposed to use fullerene molecules as weak dopants to conducting polymers[1] (CP) and found several interesting phenomena, like the quenching of photoluminescence (PL) and enhancement of photoconductivity (PC) upon doping.[2-4] originated from the photoinduced charge transfer from CP to C_{60}. Independently, similar effects of photoinduced charge transfer has been observed in different types of experiments, such as photoinduced absorption and light induced ESR.[5]

In this paper we discuss the important problems of the spectral response of the enhanced photoconductivity in different CP and its polarity effect as functions of molecular structure of conducting polymers (i.e. compare NDGS CP (conducting polymer with non-degenerated ground state) vs. DGS CP (conducting polymer with degenerated ground state)).

We present here the general scenario of photophysical processes in C_{60}/CP (conducting polymer) systems and show that photoinduced charge transfer can take place in two qualitatively different channels: either upon photoexcitation of CP or due to absorption of C_{60}.

We systematically analyse contributions to PC in each channel, emphasizing the role of self-trapping processes both in CP chains (i.e. role of intrachain and interchain exciton polarons, polarons and solitons) and in C_{60} molecules (see also this Proceedings).

The experimental results on dramatic EL quenching upon C_{60} doping are presented and compared with PL quenching.

New results on photovoltage in C_{60}/CP heterojunctions are presented in our another presentation (see this Proceedings) and analysed in terms of donor-acceptor type photocells, rather than p/n junctions.

First results on the existence of persistent photoconductivity in C_{60}/CP systems are reported and discussed in terms of creation of long lived bipolarons in C_{60} molecules under prolonged photoexcitation.

2. EXPERIMENTAL

Conducting polymers, poly(3-alkylthiophene) (PAT), poly(9,9-dialkylfluorene) (PDAFl), poly(2,5-dialkoxy-p-phenylene vinylene) (RO-PPV) and poly(o-trimethylsilylphenylacetylene) (PTMSiPA) were prepared and purified by the method already reported.[6-9] All these polymers are soluble in conventional solvents such as toluene and chloroform.

C_{60} and C_{70} prepared by an arc discharge utilizing graphite as an electrode and washed with toluene, were used in this experiment.

Both fullerene (C_{60} and C_{70}) and conducting polymer of appropriate molar ratio were dissolved in toluene, and thin films were prepared by casting the solution on an ITO (In-Sn Oxide) coated and non-coated quartz plates. Gold deposited by evaporation on the film served as a second electrode.

Layer structure of C_{60}/CP was prepared by the depositions of evaporated C_{60} on conducting polymer coated on the gold evaporated quartz plate. Then the aluminum layer was deposited by evaporation on it as a second electrode.

Absorption and fluorescence spectra were measured by utilizing a spectrophotometer Hitachi 330 and Hitachi F-2000 fluorescence spectrophotometer. Steady-state photoconductivity was measured by irradiating an Xe arc lamp light passing through a monochromator on the sample.

3. PHOTOCONDUCTIVITY ENHANCEMENT

3.1. NDGS Conducting Polymers.

In conducting polymers with non-degenerated state (NDGS CP) such as PAT, PDAFl and RO-PPV, fluorescence was quenched notably upon C_{60} doping as shown in Figur 1 for example in RO-PPV.[1-3] On the other hand, photoconductivity was enhanced intensively as also evident in Figure 1 upon amount of C_{60} doping.

It should be mentioned that the photoconductivity was enhanced in the wavelength range corresponding to (I) the inter-band transition in conducting polymer, (II) allowed

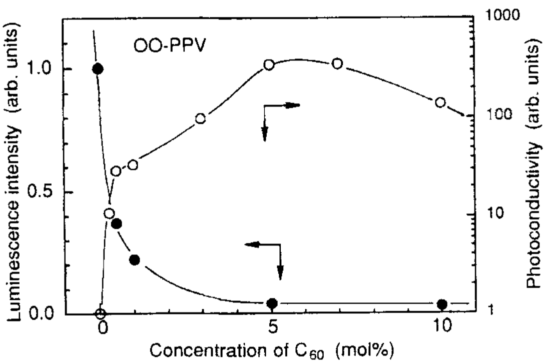

FIGURE 1 Dependence of luminescence intensity and photoconductivity of RO-PPV on the concentration of C_{60}.

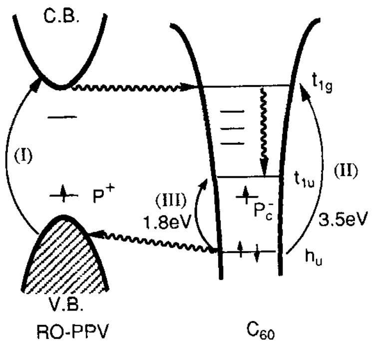

FIGURE 2 Energy diagram of OO-PPV and C_{60}.

transition in C_{60} (h_u -> t_{1g}) at 3.5 eV and also the forbidden transition in C_{60} (h_u -> t_{1u}) at 1.8 eV.

These results can be explained by the photo-induced charge transfer between conducting polymers and C_{60} as schematically shown in Figure 2. The scenario of photogeneration for NDGS CP case will be discussed in the section 3.3.

3.2. DGS Conducting Polymer

Upon doping of C_{60} the absorption spectrum of PTMSiPA film does not exhibit drastic changes characteristic to doping with conventional strong dopants such as BF_4^- . The spectrum of the C_{60} doped sample is the same with the spectrum of PTMSiPA overlapped with that of C_{60}.

Contrary to NDGS CP, quenching of photoluminescence by C_{60} doping can not be studied in PTMSiPA which has degenerated structure and shows no fluorescence even in the non-doped state. However the photoconductivity was found to be enhanced upon C_{60} doping just as in the case of NDGS CP in the wavelength also corresponding to (I) the inter-band transition, (II) excitation due to allowed transition in C_{60} and (III) forbidden transition in C_{60}.[10]

Figure 3 shows the photoconduction spectra of PTMSiPA film as function of C_{60} concentration. It should be noted in this figure that photoconductivity is remarkably enhanced upon C_{60} doping. In these spectra we can confirm a sharp peak at around 1.8eV, wide peak at around 3.5eV and also broad response in a wide band at 2.0-3.0eV. If these responses are compared with the absorption spectrum a sharp peak can be attributed to the forbidden transition of h_u -> t_{1u} in C_{60}, a wide peak at 3.5 eV to the allowed transition of h_u -> t_{1g} in C_{60} and the broad structureless response at 2-3 eV to the inter-band excitation in PTMSiPA.

3.3. Scenario of Enhanced Photogeneration Processes

The enhancement of photoconductivity can be understood from the scenario of the photogeneration and photoexcited charge transfer processes, shown at Figure 4.

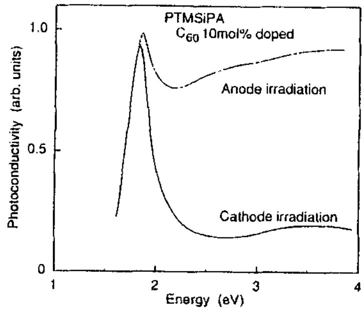

FIGURE 3 Photoconductivity spectra of C_{60}-doped PTMSiPA.

3.3.1. NDGS CP Scenario

The scenario of photogeneration is shown in Figure 4(a) for NDGS CP case. In the range (I), photo-excited intrachain exciton-polaron (Ex-P) migrates along polymer main chain and when it encounters with C_{60}, electron may be favorably transferred to C_{60} and relaxes to negative polaron (P_c^-) on C_{60}^-, which results in the quenching of photoluminescence (PL) and enhancement of photoconductivity (PC) due to the migration of positive polarons P^+ on polymer main chain. Note that in pure (undoped) NDGS CP only interchain separation of P^+ from P^- can give photoconductivity, which is rather small due to weak interchain hopping. Presence of C_{60} molecules allows electron to be captured on it, separated spatially from P^+ on the chains, which suppresses recombination and thus increases concentration of charge carriers. In the case of photo-excitation in the wavelength region (II) and (III), electron is excited from hu to t_{1g} and t_{1u}, respectively and the hole in C_{60} should be transferred to the valence band of conducting polymer (where it relaxes to P^+) which again contributes to enhancement of the photoconductivity.

It should be mentioned that direct photoinduced charge transfer from valence band of polymer to LUMO of C_{60} can take place, (see e.g. discussion in ref.12) but the energy of such CT band is apparently too low (probably in IR region) and intensity is small, and we were not able to observe it.

3.3.2. DGS CP Scenario

When C_{60} molecules are doped between chains of PTMSiPA the following two new channels open for the enhancement of photogeneration as shown in Figure 4(b):

A. C_{60} Excitation Channel: By absorbing photon of around 3.5eV, electron is excited from h_u to t_{1g} in C_{60}. The electron in t_{1g} relax to t_{1u} and should stabilize as a polaron P_c^- in C_{60} due to strong interaction with phonons or in other words due to formation of Jahn-Teller type distortion, while hole is transferred to polymeric chain. The transition from h_u to t_{1u} at 1.8eV is forbidden transition but, as we have proved for the case of C_{60} inside RO-PPV matrix still electron will be excited with some probability to h_u, due to change of C_{60} symmetry in the polymeric environment. And then it also stabilizes to P_c^- on C_{60}^-, as soon as hole from h_u level will be transferred to valence band of PTMSiPA, which should be stabilized forming charged (positive) polaron P^+. P^+ can not transfer directly to more energetically stable state of S^+ soliton due to topological restrictions but upon collision with neutral S_0 soliton, it will transform to charged S^+, which contributes to the photoconductivity. S_0 here C_{60} plays a role of "photon pump", which injects holes into polymeric chains, creating additional S^+, and thus giving rise to photoconductivity enhancement.

B. PTMSiPA Excitation Channel: By the irradiation of light with photon energy

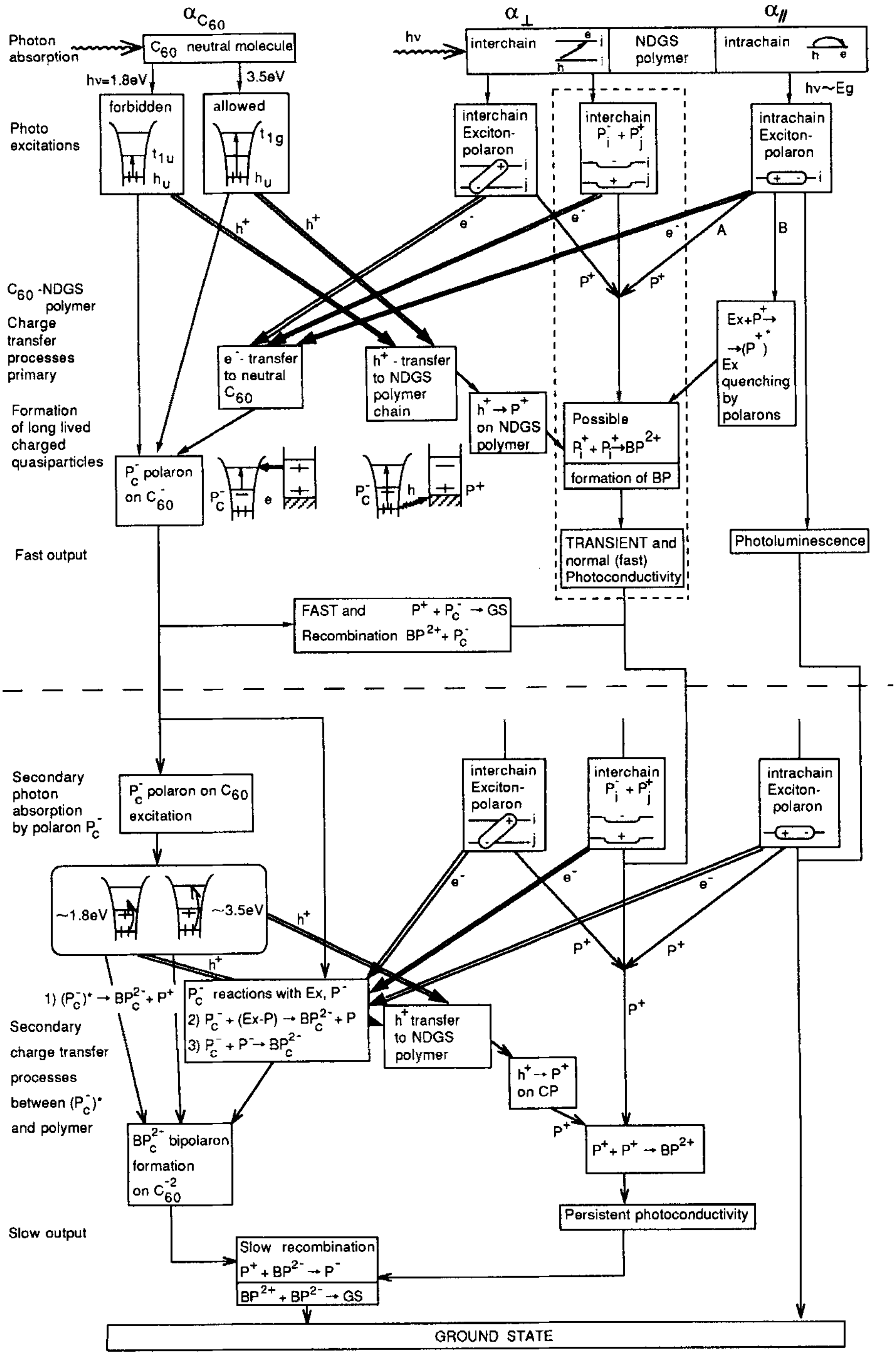

FIGURE 4 (a) The scenario of photo-induced charge transfer (PCT) in NDGS CP, senario of secondary PCT contributing to persistent photoconductivity is shown in lower part.

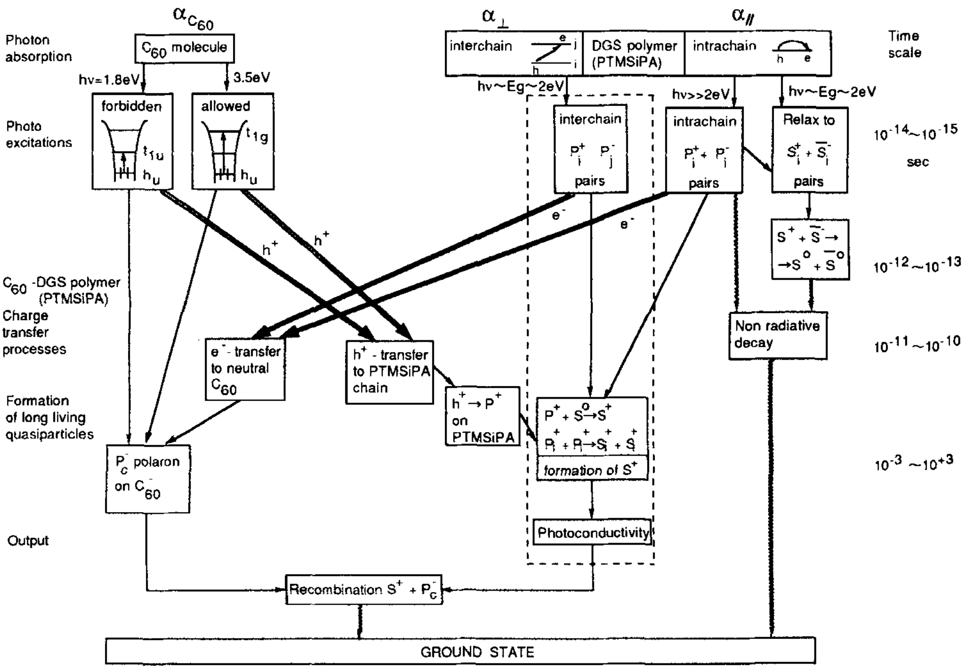

FIGURE 4 (b) The scenario of photo-induced charge transfer in DGS CP.

exceeding 2.0eV P^+ - P^- pairs should be created at adjacent chains by interchain absorption or (at hν>> 2 eV) in the same chain due to intrachain absorption in PTMSiPA and migrate along polymer main chain until meet C_{60} molecule. When the polaron P^- encounters with C_{60}, electron will be favorably transferred to C_{60} decreasing the probability to recombine with P^+, which on its turn will form S^+ through collisions with S_0 or another P^+. This S^+ will contribute to enhanced photoconductivity since the recombination of S^+ with P_c^- on C_{60}, (which is a belt-like deformation around C_{60} sphere) should be suppressed due to self trapping effects, which should decrease the overlapping between P_c^- and S^+ wave functions due to deformational and some other geometrical reasons. We shall discuss this phenomena in detail elsewhere. So P_c^- states are long living ones as has been found recently by transient-time spectroscopy by V.Vardeny *et.al.*[11]

So C_{60} plays a role of sensitizer in both NDGS and DGS CPs.

3.4. Polarity Effect on Photoconductivity

As evident in Figure 3, in PTMSiPA remarkable polarity effect was observed in the enhanced photoconductivity spectrum. That is, only for the light irradiation from positive electrode side, large signal was observed in the wavelength regions (I) and (II). However in the range of (III), for both negative and positive polarities, that is, for the excitations both from the cathode side and anode side similar magnitude of photoresponse was observed.

This is explained clearly by the migration of photo-generated positive carriers in conducting polymer, because in the ranges (I) and (II) the carrier can be only photogenerated at the area near the irradiated side electrode. The fact that the photoconductivity was observed for the case of the positive polarity means that predominant migrating carriers are positive carriers, most probably charged solitons, migrating through the bulk of the sample to negative electrode. However in range (III) carrier is uniformly generated in the bulk of sample. Therefore polarity of the applied voltage has no effect in the later case.

In the present experiment of relatively weak light intensity, the photoconductivity was linearly dependent on the light intensity.

4. PERSISTENT PHOTOCONDUCTIVITY

We have observed even at low pumping density the effect of persistent photoconductivity (i.e. the memory effect of dark conductivity enhancement due to residual charges after switching off the light source). This effect is under detailed investigation currently. It is found that after switching off the light source the dark conductivity is enhanced by some amount, depending on the spectral range used for photoexcitation. Annealing to rather high temperatures can restore the initially low dark conductivity, confirming that charges are accumulated in some deep traps, meaning that recombination of charges is strongly suppressed.

Typical photoconductive response in C_{60} doped PAT-18 upon irradiation of light pulses of 1.8 eV in photon energy is shown in Figure 5. Similar behavior was also observed upon excitation with photons of 2.2 eV and 3.5 eV. As evident in this figure, the photoresponse was found to be composed of two parts; a fast part and a slow part. That is,

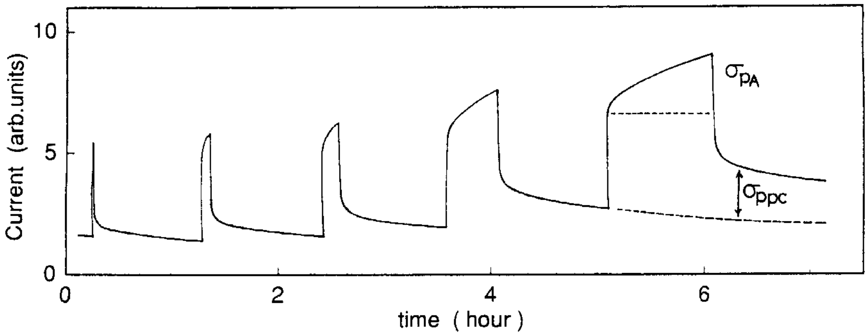

FIGURE 5 Typical photoconductive response in C_{60} doped PAT-18 upon irradiation of light pulses (1.8 eV).

upon irradiation of a light pulse photoconduction increases in step wise then continues to grow slowly during the pulse width of light. Upon shutting off the light, the photocurrent decreases by some amount in step-wise and then the remaining part decreases very slowly. That is, the decay time of remanent component is extremely long compared with the prompt component. This remanent component of photoconductivity can be called as a persistent photoconductivity (σ_{PPC}). Therefore, the slowly increasing part of photoconducting under the pulse light irradiation may be originated in the accumulation of persistent photoconducting carriers (σ_{PA}). This interpretation is consistent with the pulse width dependence of photocurrent as shown in Figure 5. As evident in this figure, the slow rising component σ_{PA} increases as the pulse width increases and the persistent conductivity σ_{PPC} also increases. This pulse width dependence of the persistent conductivity is more clearly shown in Figure 6, in which the persistent conductivity is evaluated at 5 minutes after the stop of light irradiation.

The existence of persistent photoconductivity means that the recombination probability of the separated positive (in PAT-18) and negative (in C_{60}^-) charges is strongly inhibited limited. There seems to be several possibilities for the suppression of the recombinations;

(1) Change of the charge distribution in C_{60}^- from the initially captured state, that is, rotation of charge belt, resulting in the smaller overlapping interaction with main chain π system. (2) The further stabilization of C_{60}^- to C_{60}^{2-} bipolaron BP_c^{2-}. (3) The disorder of the conformation of polymer main chain and resulting fluctuation of the electronic band scheme of CP with long side chain may also contribute for the suppression of the recom-

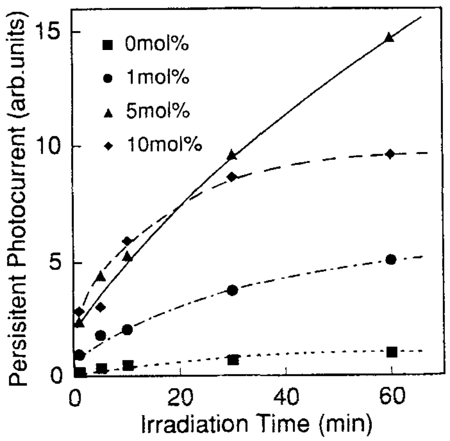

FIGURE 6 Pulse width dependence of the persistent conductivity of doped C_{60} PAT-18.

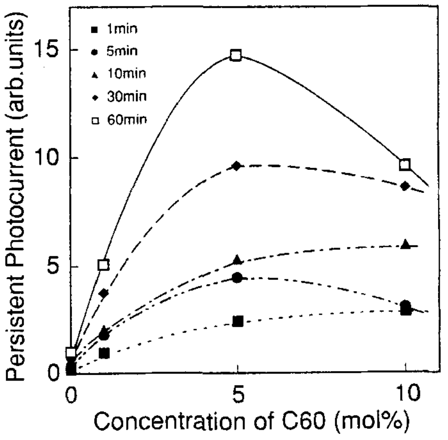

FIGURE 7 Dependence of persistent photoconductivity of PAT-18 on the concentration of C_{60}.

bination of separated carriers. Some of scenario of persistent PC is shown in the lower part of Figure 4(a) below dashed horizontal line.

The magnitude of persistent photoconductivity increases with increasing concentration of C_{60} as shown in Figure 7. However at higher C_{60} doping level, it tends to saturate (or decrease again). Dependences of persistent photoconductivity on light intensity and also temperature were also studied. With increasing light intensity, persistent photoconductivity increases, tending to saturation. At higher temperature, the persistent photoconductivity in PAT-18 is found to tend to decrease.

5. ELECTROLUMINESCENCE QUENCHING

Recently, conducting polymers such as poly(p-phenylene vinylene), poly(3-alkylthiophene), poly(9,9-dialkylfluorene) and poly(p-phenylene vinylene) derivatives have been demonstrated to be used as active light emitting layer in EL(electroluminescence) diode by sandwiching with cathode and anode electrodes. We already reported that molecularly doped conducting polymer exhibits also unique characteristics as the light emitting layer in a EL diode. We have also studied effects of C_{60} doping on emission characteristics of EL diode based of conducting polymer.

EL is also found to be quenched upon C_{60} doping as shown in Figure 8 for example in the EL diode of Mg-In/OO-PPV/ITO structure, though the emission spectrum does not show notable change. It should be noted in this figure that EL quenching by C_{60} is much more dramatic than PL quenching. That is, upon doping of 2 mol% of C_{60}, PL intensity

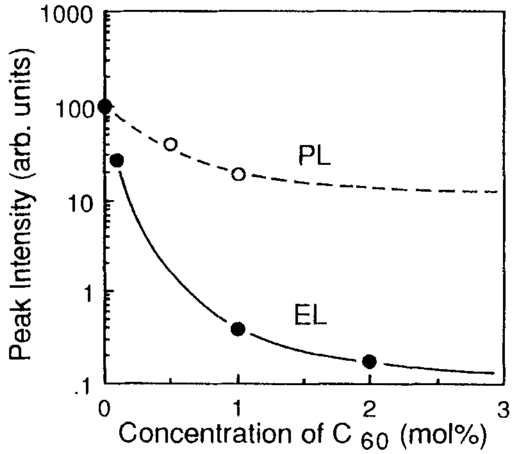

FIGURE 8 Dependence of electroluminescence and photoluminescence intensities on the concentration of C_{60}.

was quenched to about 20 % of that in non-doped OO-PPV. On the other hand, upon doping of 2 mol % of C_{60}, EL intensity was quenched to less than 1% of that in the non-doped EL diode at room temperature.

The stronger EL quenching can be explained by taking the process of EL emission into consideration as follows.

In conducting polymer EL diode, electrons (or negative polarons P^-) and holes (or positive polarons P^+) are injected into conducting polymer from the cathode and the anode, respectively. Either one type or both types of carriers migrate crossing electrode distance under biased electric field. Upon encountering of electrons (P^-) to holes (P^+), excitons (actually self-trapped exciton-polarons, which we denote for simplicity as Ex) will be formed and the radiative decay of those excitons is the origin of the EL emission.

Therefore, C_{60} doped in conducting polymer may play a complicated role: (1) induce dissociation of Ex, and (2) capture (trap) carriers (either both P^- and P^+ or one of them). The existence of the second process may be the origin of stronger quenching effect in EL than in PL.

We have studied EL quenching effect for EL diodes with different thickness of conducting polymer layer. In general, EL emission intensity from thicker EL diode was smaller than that from thinner one under the same diode current. However, it should be mentioned that the EL quenching effect did not depend on the thickness. That is, the quenching ratio of EL intensity was just the same for different thickness of EL diodes.

These results can be explained with the transfer of only one type of carriers namely P^+ across the electrode distance, since most conducting polymers are known to be unintentionally p-type semiconductor by residuals of catalysts or other impurities.

The fact that, EL quenching effect by C_{60} is not influenced by the thickness of conducting polymer suggests that only one type of carrier transits between electrodes and it is not trapped by C_{60} before encountering with opposite polarity of charge and forming of excitons. Therefore, excitons must be formed in the area near one of two electrodes, resulting in EL emission from this area. In most conducting polymers, majority photo carriers are positive carrier (holes or P^+). Then it is reasonable to consider that holes (P^+) transit from the anode to the cathode without severe trapping by C_{60} and forming excitons at the area near the cathode. This is in consitent with electronic band schemes, according to which HOMO of C_{60} (h_u-level) is much lower than top of the valence band and electronic level 0 of P^+ in RO-PPV, making hole transfer to it unfavorable.

On the other hand, electrons (or P^-) can be captured by C_{60}, because the conduction band bottom (LUMO) of RO-PPV is located at energy higher than the LUMO (t_{1u}) of C_{60}. Therefore, the experimental results suggest that the injected electron (P^-) from the cathode are effectively captured by C_{60} forming C_{60}^- (or actually the negative polaron of the belt type deformation around the perimeter of C_{60} sphere) during migration of short distance before encountering hole (P^+), effectively resulting in the formation of smaller density of excitons at the area near the cathode. Even if Ex has a chance to be formed it should also be dissociated by the interaction with neutral C_{60} or its ions C_{60}^{n-}. It is also probable that even polaron on C_{60}^- (P_c^-) may capture second electron, since according to numerous theoretical predictions two electrons prefer to occupy the same C_{60} rather than two different molecules, forming dianion or bipolaron BP_c^{2-}, C_{60}^{2-}, either due to effectively negative Hubbard U or/and due to stronger self-trapping effect. Due to very strong electron accepting ability (and as recently proved, C_{60} can accept up to 10 electrons from alkali metals) it is not excluded at the present stage that even third, forth and n-th electrons can be captured by the same C_{60} molecule forming C_{60}^{3-}, C_{60}^{4-}, C_{60}^{n-} respectively. These facts indicates that C_{60} may be very strong multiple trapping center for carriers, which to our knowledge was not observed for any other impurities. That is the power of C_{60} as electron trapping center may be extremely high exceeding any known up to now centers.

It should be mentioned that C_{60}^{n-} formed by capturing negative carriers can then be extremely effective recombination center for holes (P^-) due to unusually strong Coulomb attraction between them, n-times enhanced. By this non-radiative recombination, C_{60}^{n-} turns to C_{60} and becomes again effective trap for electrons. Very roughly speaking ,if this picture is true, then C_{60} at concentration m% acts effectively as at concentration of (nm)%, due to its multiple trapping effect, i.e. effect of each C_{60} is n-times enhanced. This picture needs further investigation, since due to charging of C_{60} one should consider space charge limited current in EL diode in multiple charging limit.

Anyway the C_{60}/conjugated polymer EL diode may serve as an ideal system to study the multiple charging effect on C_{60}, and especially to check the existence of BP^{2-} which are believed to play a important role in superconductivity of alkali-metal fullerides.

It can be controlled by injecting P^- at different conditions into EL diode and probing charged BP_c^{2-} andC_{60}^{n-} multianions by various modulation spectroscopy methods. This work is in progress currently.

6. DISCUSSION

Let now summarize of our study of C_{60}- conjugated polymer composites. We have demonstrated above that C_{60} is an example of so called weak dopant, or in other words "photodopant", which can transfer the charge to the polymeric chain upon photoexcitation even if it was impossible in the ground state (i.e. in dark conditions).

The steady state density of holes in CP chains responsible to enhanced PC is determined by several factors, excitation probability, collision probability of exciton with C_{60}, charge transfer probability between CP and C_{60}, and recombination probability between positive carrier in CP and negative polaron in C_{60}.

The suppression of recombination is apparently strongly enhanced by the self-trapping effects both in polymer (in which charges are relaxed into deep states of polaron/bipolarons or solitons) and in fullerene, where a belt-type atomic deformation along the perimeter of C_{60} sphere is known to exist, due to Jahn-Teller effect on triply degenerate t_{1u} level. This later effect of relaxation needs more theoretical understanding, but the effect of persistent photoconductivity observed here implies that this self trapping is an important phenomena.

Another possibility to enhance PC due to increased interchain mobility of P^+, due to C_{60} mediated interchain hopping exists and is analyzed in our paper in this Proceedings.

Actually in this general problem of weak dopant which exhibits strong self-trapping there are many questions that need more deeper understanding and thus more experimental study to clarify carefully each step of the process of charge separation and relaxation. Let here point out some of this important steps:

A. Photoluminescence and Electroluminescence Quenching: We have mentioned above only one possible source of PL quenching due to dissociation of exciton-polaron (Ex-P) with electron transfer to neutral C_{60}: $Ex + C_{60} \rightarrow P^+ + C_{60}^-$. As noted in our earlier paper, one can not exclude at present stage that the transfer of excitation energy due to dipole-dipole Förster type interaction also contributes to PL quenching: $Ex + C_{60} \rightarrow (C_{60})^*$, where $(C_{60})^*$ defines excited state of neutral C_{60} molecule (which exhibited $h_u \rightarrow t_{1u}$ transition, that becomes allowed in polymeric matrix. As we found in our preliminary results on the existence of persistent photoconductivity, C_{60}^{n-} cations P_c^-, BP_c^{2-} and BP^{2+} are longly living states and after their accumulation new channels for nonlinear PL and EL quenching may open. Firstly Ex may interact with P^+ and transfer energy to P^+ as already observed in nonlinear PL quenching in pure PPV upon high density of photopumping: $Ex + P^+ \rightarrow (P^+)^*$, The theory for this Ex decay reaction has been proposed already although it is not understood completely. Note that if initially P^+ is bound to C_{60}^- by Coulomb attraction, then in $(P^+)^*$ excited state it may become free giving rise to additional nonlinear enhancement of photoconductivity, which may be observed at high light intensity.

Another new possibility is the interaction of Ex with persistent P_c^- on C_{60}^-. Two processes may contribute to such interaction:

1) $Ex + C_{60}^- \rightarrow C_{60}^{2-}$, the formation of BP_c^{2-} on C_{60}, since C_{60} is a good acceptor, which can accept up to 10 electrons. This BP_c^{2-} can be long living state as thus give rise to the observed effect of persistent photoconductivity, since each BP_c^{2-} effectively creates additional mobile long lived P^+ (due to neutrality).

Also the back transfer of electron to Ex can not be excluded:

2) Ex + C_{60}^{-} -> P^{-} + C_{60}, so the careful study of time dependences and high optical pumping ESR and PC are required to clarify which of this interesting reactions between Ex and C_{60} takes place. We discussed in detail in Sect.5 other EL quenching chanells.

B. Photoconductivity Enhancement and Persistent Photoconductivity: In our simple explanation above the enhancement of photoconductivity comes from the suppression of recombination of P^{+} and P_c^{-}, due to their spatial separation. However we have not considered the special role of self-trapping effect. Here it should be mentioned that due to the belt type one-dimensional nature of P_c^{-} in C_{60} the overlapping of wave functions of P^{+} (in CP chains) and P_c^{-} can be strongly changed due to geometrical reasons, depending on the relative orientation of the belt (ring) to the π-orbitals on conjugated segment of the chain which contains P^{+}. It has been shown recently by Yu Lu et al. (see this Proc.) that in polaronic state P_c^{-}, the belt is not fixed and tunnels between six equivalent positions. However in bipolaron BP_c^{-} the belt is spatially fixed due to stronger self-trapping effect, which means that overlaping of BP_c^{-} wave function with the chain is more suppressed than in case of P_c^{-}. This stronger suppression of overlapping may be the reason for the observed persistent photoconductivity, since charges in C_{60} belt P_c^{-} may live long time, while P^{+} should contribute to dark conductivity being not able to recombine with P_c^{-} due to negligible overlapping of their wave functions.

Another point which needs careful understanding is the Coulomb attraction of P^{+} to P_c^{-}: simple estimates show that at 4 Å separation between C_{60} and CP chain the binding energy may be as large as 0.2 - 0.4 eV, meaning that at small C_{60} concentrations main part of P^{+} should be bound at room temperature to P_c^{-}. Probably the excess of kinetic energy which P^{+} has after the dissociation of Ex, or after hole transfer from C_{60} is enough to avoid binding at the first stage, while interaction with Ex may provide a source of kinetic energy helping to unbound P^{+} at later stage.

Anyway the careful study of persistent photoconductivity and effects of high photopumping are in progress now to understand the origin of PC enhancement and its time evolution. One should note that the mobility of P^{+} also may be enhanced by C_{60} dopants (see this Proceedings).

It should be mentioned also that unique junctions such as photo-sensitive diode and FET whose characteristics are controlled by light irradiation can be fabricated utilizing CP doped with fullerene such as C_{60} as photo-dopant and are now under study.

7. SUMMARY

Novel charge transfer (CT) controlled effects, either by electrode injection, such as quenching of electroluminescence, or photo-induced C_{60} - CP charge transfer, such as quenching of photoluminescence, enhancement of photoconductivity and its persistent component are found in C_{60} doped conducting polymer and also C_{60}/conducting polymer EL diodes. The results are explained by taking into account the electronic energy states of C_{60}, corresponding to so called weak acceptor, whose LUMO level, namely t_{1u} lies within the energy gap of conducting polymer. The dynamics of self trapped excitations: exciton-polaron and polaron in conducting polymers with non-degenerated ground state and solitons in the conducting polymer with degenerated ground state, together with polaron in C_{60} molecule is shown to be important for the processes of charge separation and re-combination, enhancing the number of photogenerated carriers, which have rather long life time, as confirmed by observation of persistent photoconductivity.

ACKNOWLEDGEMENT

Part of this work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 04205097) from the Ministry of Education, Science and Culture. A.A.Z. is thankful for the hospitality of Osaka University and support of Uzbek Fund of Fundamental Research under grant 12.

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