



DOPING EFFECT OF BUCKMINSTERFULLERENE IN CONDUCTING POLYMER: CHANGE OF ABSORPTION SPECTRUM AND QUENCHING OF LUMINESCENCE

Shigenori MORITA, Anvar A Zakhidoy* and Katsumi YOSHINO

Faculty of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, JAPAN

*Permanent address: Department of Thermophysics, Uzbek Academy of Science,
Katartal 28, Chilanzar, C. Tashkent, Uzbekistan, CIS.

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Buckminsterfullerene(C_{60}) is found to be an effective dopant for poly(3-alkylthiophene). Inter-band absorption of poly(3-alkylthiophene) has been remarkably suppressed and blue shifted and new absorption peak evolve in the low energy range upon doping by C_{60} . From a consideration of the energy diagrams, the electron transfer from poly(3-alkylthiophene) to C_{60} is proposed to be favorable in energy at account of Jahn-Teller splitting of LUMO in C_{60}^{-1} state or/and the Coulomb attraction of positively charged polaron P^+ to C_{60}^{-1} . The suppression of photoluminescence(PL) in poly(3-alkylthiophene) upon doping by Buckminsterfullerene has also been observed confirming the doping effect. The nonradiative decay of excitons due to interaction with P^+ introduced by doping is discussed as the origin of such PL quenching.

1. INTRODUCTION

Recently C_{60} named also as Buckminsterfullerene has attracted great interest as a new type of exotic π -conjugated all carbon molecule. It exhibits not only unique spheric molecular structure but also in solid state shows superconductivity with relatively high critical temperatures upon doping by alkali metals: M_3C_{60} ($M=K, Rb, Cs$)[1-3] and even ferromagnetic behavior[4] in the complex with organic donor TDAE. Surprisingly doped C_{70} and other higher fullerenes C_n ($n=76, 78, 84, 90$, etc.) do not show neither superconductivity[5] nor magnetic ordering[6] suggesting somewhat exceptional properties of C_{60} in the fullerenes family. It is interesting therefore to investigate other properties of this unique molecule. So we have recently indicated that visible electroluminescence may be obtained in the Buckminsterfullerene diode with clear rectifying properties.[7]

On the other hand conducting polymers have attracted much interest due to drastic changes of electrical, optical and magnetic properties upon doping. Introduction of new concepts such as soliton, polaron and bipolaron to explain these unique characteristics[8] and proposals of various applications of conducting polymers have stimulated synthesis of new conducting polymers and the search for new effective and stable dopants.[9-12]

Among various conducting polymers, poly(3-alkylthiophene) (PAT) has attracted much attention as soluble and even fusible polymer because it exhibits interesting novel properties such as thermochromism[9], solvatochromism[10], gel chromism[11] and anomalous luminescence[9]. In this polymer, the average conjugation length L and hence the band gap E_g and inter-chain distance were found to depend on the length of alkyl side chain.

So far various molecules and compounds have been used as p-type dopants in conducting polymer such as halides,

metal halides, Lewis acids, etc.[8] The size of dopant so far studied is relatively small except for several cases such as phthalocyanine and $B_{10}Cl_{10}$ [12]. In the later case of a larger size dopant the stability of doping has been found to increase and the search for new large dopants seems to be quite important.

The ability of C_{60} to withdraw up to six electrons from alkali metal dopants (e.g.: in insulating M_6C_{60} , $M=K, Rb, Cs$, etc.) reflects its very large electron affinity and suggests the possibility to use it as an acceptor for organic solids and conducting polymers especially.

In this paper, we report that C_{60} can be used as p-dopant in conducting polymer matrix while being n-type doped itself, that is, electron is transferred from polymeric chain to LUMO of C_{60} charging it to C_{60}^{-1} ionic state and creating positively charged polaron P^+ in PAT chain. The photoluminescence in PAT is shown to be remarkably suppressed and absorption spectra dramatically changed upon C_{60} intercalation confirming the doping effect.

2. EXPERIMENTAL

PATs were prepared utilizing $FeCl_3$ as a catalyst. Details of the preparation and purification method and procedure were already reported in our previous papers.[10,13] Among various PATs, in the paper mainly the results obtained utilizing poly(3-hexylthiophene) were discussed. However, other PATs with different alkyl chains exhibited similar characteristics.

Buckminsterfullerene prepared by the wellknown method by an arc discharge from graphite and washing with toluene, and provided by Science Laboratories Co., Ltd. for the experiment.

Both PAT and C_{60} of appropriate molar ratio were dissolved in common solvent, toluene. Then thin films were prepared by casting the solution on appropriate substrates such as glass and quartz plates.

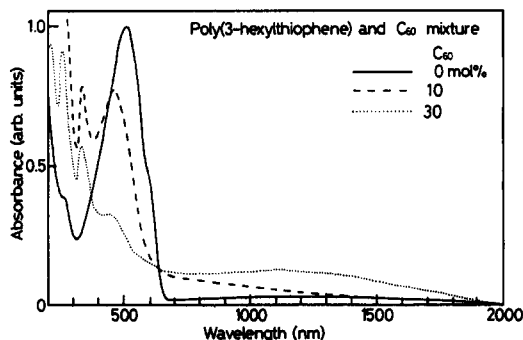


Fig.1. Absorption spectra of poly(3-hexylthiophene) with various concentration of buckminsterfullerene.

Absorption spectrum was measured utilizing spectrophotometer (Hitachi 330). Photoluminescence was measured utilizing a lock-in-amplifier system. An Ar ion laser(488.0nm) was used as the exciting light source for photoluminescence measurement. Details of apparatus and method for the measurement of luminescence were already reported in our previous paper.[14]

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of PAT films doped with various concentration of C_{60} . As evident from this figure, high energy peak originating due to the inter-band transition was suppressed upon doping. On the other hand, new absorption peak was found to evolve in the near infrared region around $E=1.1\text{eV}$ with increasing concentration of C_{60} . Note that another new absorption peak at energy higher than band-to-band transitions of PAT can be observed only at high concentrations of C_{60} and it is nothing else but the absorption of C_{60} itself since is in excellent correspondence with similar shape peak at 3.6 eV in solid C_{60} films.[15]

Figures 2 and 3 demonstrate the dependence of the intensity of the absorption peak of the inter-band transition and the shift of wave length of this peak on the concentration of C_{60} .

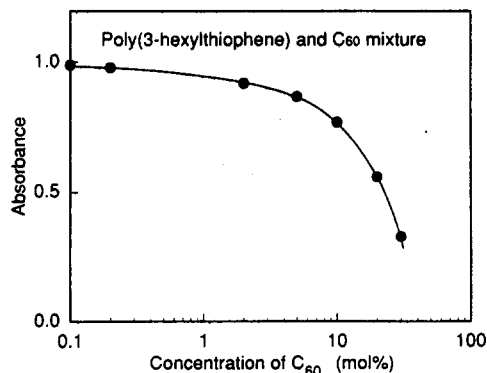


Fig.2. Dependence of the intensity of absorption peak of poly(3-hexylthiophene) on the concentration of Buckminsterfullerene.

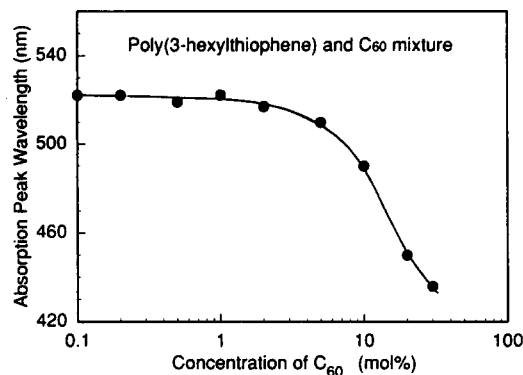


Fig.3. Dependence of the wave length of absorption peak of poly(3-hexylthiophene) on the concentration of Buckminsterfullerene.

Similar suppression and blue shift of the inter-band absorption and evolution of low energy peaks were observed in PAT upon doping with conventional dopants such as BF_4^- etc.[8,16]

These observations clearly support that PAT can be effectively doped with C_{60} . The suppression of the inter-band absorption should be explained by the transfer of electrons from the conjugated chain of PAT to C_{60} . Upon this charge transfer the polymer conjugated system should be dramatically modified and distorted due to the strong electron-lattice interaction in one-dimensional system and polarons P^+ or bipolarons BP^{2+} should be formed. Therefore the density of states in the upper energy range of the valence band must be decreased, resulting in the suppression of the inter-band absorption especially in the lower energy part. This interpretation is just the same as in the case of electrochemically doped polythiophene. The absorption peak in the low energy range can be interpreted in terms of optical transition related with P^+ state as in the case of low concentration of conventional dopants. However, it should be noted that at low doping stage by C_{60} , the low energy peak is not significantly intensive contrary to the case of doping by conventional dopants such as BF_4^- of the same concentration. The low energy peak only becomes remarkable at high doping level and the energy of the peak in this case is slightly different from P^+ state created by BF_4^- doping. This fact suggests the influence of the large, highly polarizable C_{60} either on the conformation of polymer chains i.e. on the electron-lattice interaction and therefore the formation of polaronic states, or otherwise reflects some other types of interactions of polarons with C_{60} as discussed below.

The electron transferred to C_{60} should also form the negative polaron ($P_{C_{60}}^-$) on C_{60} molecule (see discussion below) optical transitions to which levels are expected at 0.7 eV [17] and should overlap with the P^+ transitions and thus also contribute to wide intragap absorption observed here. Note that even at highest available concentration of C_{60} (~30mol%) the second intragap peak known for bipolaronic (BP) transition [8,16] never appeared, suggesting that effectively the doping level is low enough and no formation of BP can thus be observed.

The effective doping of C_{60} in PAT is also reasonable

from the consideration of the electronic energy diagrams of PAT and C_{60} .

To obtain this energy band diagram of C_{60} -PAT system one needs the values of vertical ionization potential $I_p = I_0 + P_e$ and bandgap E_g of C_{60} inside the PAT matrix. Here, I_0 is the molecular ionization potential and P_e the polarization energy. Since the exact data for I_p and E_g are not available yet (now upon measurements) the published data of $I_p = 6.8\text{ eV}$ [18] for solid C_{60} can be used as good approximation since P_e should not be too much different for solid C_{60} and C_{60} in PAT matrix as far as both are polarizable π -conjugated solids for which P_e usually has close values. Taking the value of direct bandgap (involving forbidden transitions) as $E_g = 1.5\text{ eV}$ as calculated [19] and recently observed in photoconductivity [20] we arrive to the band scheme of Fig.4. The positions of bands and bipolaronic levels of PAT have been obtained earlier [16] using the photoemission data. As can be seen the top of valence band of polymer is only slightly $\sim 0.2\text{ eV}$ lower than the bottom of conduction band of solid C_{60} (or as we assume here as LUMO of C_{60} inside polymer). This value becomes a little higher if we estimate $E_g = 1.6\text{ eV}$ as found in [21] from the optical absorption of C_{60} films using the photothermal deflection spectroscopy. So the transfer of free electron between the rigid bands of C_{60} and PAT hardly seems to be possible since charge transfer (CT) requires the positive energy $\delta_{CT} = 0.1\text{--}0.2\text{ eV}$.

However the charge transfer from polymer to C_{60} may occur if the polaronic effects are taken into account both in polymer (P^+ level $\sim 0.2\text{ eV}$, while $BP^{2+} \sim 0.7\text{ eV}$ above the valence band top [16]) and also in C_{60} molecule: [17] in which the shape deformation effect is also expected [17,22] leading to splitting of 3-fold degenerate LUMO of C_{60} in ionic state due to polaronic distortion [17] or in other words Jahn-Teller distortions [22,23]. In the latter case the t_{1u} level should be split to 3 levels of different symmetries as sketched at Fig.4, and transferred electron should occupy the lowest of split levels which is significantly lower than LUMO of neutral C_{60} and estimated energy gain ranges from $E = 1.0\text{ eV}$ [23] to $0.06\text{--}0.08\text{ eV}$ [17] in different models. Moreover it has been shown earlier [24] that in the case of weak dopants with slightly positive CT energy the Coulomb attraction of the P^+ to the dopant (in our case

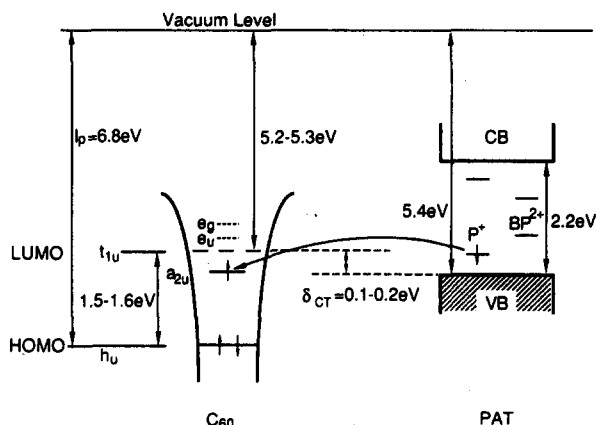


Fig.4. Energy diagram of poly(3-alkylthiophene) and Buckminsterfullerene.

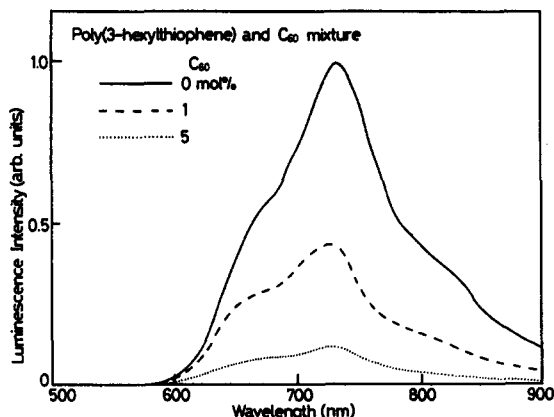


Fig.5. Photoluminescence spectra of poly(3-hexylthiophene) with various concentration of Buckminsterfullerene.

estimated as $V_c \sim 0.3 - 0.5\text{ eV}$) can additionally stabilize the charge transfer due to P^+ binding to dopant. So doping can become possible also due to creation of polarons P^+ in the bound state with C_{60} ; even if Jahn-Teller or polaronic gain (which is not still found experimentally) is not large enough as e.g. estimated in [17].

Bipolaronic doping with creation of BP^{2+} and C_{60}^{2-} also cannot be excluded at present at much higher dopant concentrations since the Hubbard repulsion of two electrons on large C_{60} molecule may be significantly suppressed. To check this possibility the ESR measurements are in progress now together with conductivity measurements.

Quenching of photoluminescence was also confirmed in PAT upon doping by C_{60} .

As shown in Fig.5, the photoluminescence spectra of PAT changed drastically upon doping of C_{60} . That is, the intensity was suppressed remarkably and also blue shift of the emission peak was observed. The blue shift of the photoluminescence peak can be explained by the decrease of the density of states at the top of valence band and

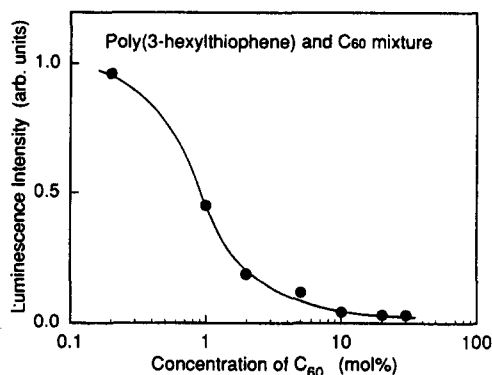


Fig.6. Dependence of luminescence intensity of poly(3-hexylthiophene) on the concentration of Buckminsterfullerene.

resulting increase of effective band gaps as discussed in the change of absorption spectrum.

Figure 6 shows the dependence of luminescence intensity on the concentration of C_{60} . The intensity was suppressed remarkably even at dopant concentration less than 1%. The dopant concentration at which suppression of photoluminescence became remarkable is much lower than that of the absorption change.

The suppression of photoluminescence in conducting polymer was found at the first time in iodine doped cis-polyacetylene by the author.[25] Then similar phenomena were found in the electrochemically doped polythiophene.[26] The suppression of photoluminescence upon doping can be explained by the non-radiative decay of photo-created excitons when they encountered with polarons as already proposed by the author.[26,27] The microscopic mechanism of intrachain nonradiative decay of excitons due to formation of $Ex+P^+$ bound state has been recently studied theoretically [28] while the possibility of interchain nonradiative decay of Exciton due to energy transfer to P on the adjacent chains has also been mentioned.[29]

The details of interpretation of the mechanism of the suppression of photoluminescence are now under study.

Summarizing we have found that electron transfer occurred from PAT chains to C_{60} molecule with formation of P^+ -polarons as observed in changes of inter-band and intragap optical absorption and photoluminescence quenching. However comparatively low intensity of the intragap polaronic transition even at high concentration of C_{60} (>20mol%) suggests that all intercalated C_{60} molecules may not be charged, and some molecules of C_{60} can be still in the neutral state. One can propose that only C_{60} at shortest distances to PAT chains are charged, due to largest Coulomb stabilization of P^+ , while more distant C_{60} having larger separation positions due to existence of long alkyl side chains of PAT are probably neutral. Even these neutral C_{60} molecules can contribute to PL-quenching acting as weak dopants [24] to which either charge or excitation can be transferred only upon photoexcitation followed by nonradiative decay. Preliminary measurement of ESR also support the effective doping of C_{60} in PAT. That is, ESR line width in C_{60} doped state (2G at 20mol% doping) was much narrower than that of undoped polymer(7G).

The possibility to intercalate large C_{60} molecules into polymeric matrix may have interesting applications for batteries and volume changeable devices like actuators.

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