Photoluminescence studies on [C60] fullerene solutions in N-methyl-2-pyrrolidinone and pyrrolidine

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PHOTOLUMINESCENCE STUDIES ON [C60] FULLERENE SOLUTIONS IN N-METHYL-2-PYRROLIDINONE AND PYRROLIDINE

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Photoluminescence (PL) spectra of C_{60} solutions in N-methyl-2-pyrrolidinone (NMP) show a drastic increase of the PL intensity if the solutions are stored longer periods of time. Two distinct spectral components, one in the red (1.92–2.00 eV) and another in the green (2.18–2.3 eV) were identified in the whole PL emission. Their weights depend on C_{60} concentration and on storage time. The two emissions come from two successive processes running with different kinetics. Charge transfer, leading to (C_{60},NMP) loose molecular complexes and a slow aggregation process of these entities seems to originate the red and green emission, respectively. Similar PL properties are found when pyrrolidine (P) is used as solvent.

Keywords: [C60]fullerene; N-methyl-2-pyrrolidinone; photoluminescence; pyrrolidine

1. INTRODUCTION

[C60] fullerene in solution exhibits several inciting properties. Among these the aggregation of C_{60} in single and binary solvent mixtures is one of the most intensively studied [1–8]. Genesis of stable self-assembled fullerene aggregates is accompanied at least in nonpolar-polar solvent mixtures by a dramatic solvatochromism [4,6]. Despite of some significant changes in

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absorption spectra, the emission properties of C_{60} in cluster form are usually found in close resemblance with those corresponding to nonaggregated [C60] fullerene, almost all reports showing an emission band at about 700 nm (1.77 eV). Because of a very efficient intersystem crossing [C60] fullerene is weakly fluorescent; a quantum yield of only 3.2×10^{-4} was found at room-temperature in toluene solution [9]. On the other hand, due to its electrophilic character [10,11], C_{60} can form in solution charge transfer complexes with a variety of inorganic and organic electron donors. Special attention was paid to the complexes formed with various aliphatic [12] and aromatic amines [13,14]. Moreover, C_{60} is able to form molecular complexes not only with well-known electron donors but even with the solvent molecules [15–17].

The strength of intermolecular interaction solute–solvent plays a crucial role in all these properties. As a result, some particularities of C_{60} behavior are expected in nucleophilic solvents where beside the week Van der Waals type forces other stronger forces of chemical origin can act, in relation to a charge transfer between fullerene as acceptor and solvent molecules as donor. Just few data were reported about the PL behavior of C_{60} solutions in such nucleophilic solvents [17].

In this work we have focused on PL properties of C_{60} solutions in N-methyl-2-pyrrolidinone (NMP) and pyrrolidine (P). Solutions with different C_{60} concentrations and films prepared from them were used in this study. PL spectra were systematically recorded over a long storage time of solutions extended up to two years. We show that the dramatic changes in PL spectra originate in two successive processes ending in stable molecular aggregates where [C60] fullerene is linked to solvent molecules.

2. EXPERIMENTAL

The solvents and C_{60} powder used in this work were of Merk quality without further purification. Solutions with different concentration of C_{60}, in the range of 0.2–2 mg/ml were prepared by dilution starting from a solution with a content of C_{60} of 2 mg/ml. After preparation the solutions were ultrasonically homogenized for few minutes and hermetically bottled in quartz cells. The PL measurements on solutions and films samples were performed at room temperature both immediately after the preparation of solutions and after different storage times. The films used for PL measurements were deposited on quartz supports by the evaporation of the solvent. PL records were obtained in a backward geometry using a computer controlled emission spectrometer consisting from a SPEX double monochromator equipped with a cooled EMI photomultiplier and a photon

counting system. Laser line of 457.9 nm from Coherent Innova 90 argon ion laser was used as excitation light.

3. RESULTS AND DISCUSSION

For comparison we present the PL behavior of C_{60} solution in a common fullerene solvent as 1, 2-dichlorobenzene (DCB). In Figure 1A the PL spectrum of a fresh prepared solution with a fullerene content of 0.4 mg/ml is shown. Subtracting the solvent emission, depicted in inset, one obtains an emission band with the peak position at about 1.77 eV typical of weak fluorescence of solvated [C60] fullerene. No relevant differences in the emission spectra were observed if the solution was left standing longer period of time although an aggregation process of fullerene as in other aromatic solvents was assumed to take place. This result shows once more that the formation of nanometer size clusters in widely used fullerene solvents involves just weak interball interactions, of Van der Waals type, that cannot significantly alter the emission characteristics of [C60] fullerene.

If NMP is added at such C_{60} solution in DCB, drastic changes in PL spectra are observed with the increase of the storage time. In Figure 1B we present the modification of emission spectra corresponding to a [C60] fullerene solution in NMP: DCB mixture with the solvent volume ratio of 1:5. From bottom to top are shown the PL curves recorded for fresh and one and two years stored solutions, respectively. Concentration of C_{60} in the solvent mixture was preserved at the same value of 0.4 mg/ml. The solution storage leads to a spectacular increase of emission intensity in PL spectra. At a shorter storage time the enhancement of intensity is accomplished especially by an emission in the red with the peak position at about 1,92 eV. The development of an additional emission ranging in the green, with its peak at about 2.25 eV is observed at longer storage time. Inevitably, all these changes in PL spectra, deriving from [C60]fullerene-NMP interaction must be finally related to nucleophilic properties of NMP molecules. We should also remark that the two spectral distinct components, further labeled as the red and green emission originate in slow rate processes. The statement is supported by the persistence in the emission spectra for a longer period of time of the band peaking at 1.77 eV interpreted in this case as signature of non-interacted C_{60} molecules.

Passing over to C_{60} solutions in single NMP, the variation of PL spectra with storage time, for two solutions of different C_{60} concentration, 2 and 0.5 mg/ml, is presented in Figure 2A1 and Figure 2B1, respectively. Curves 1 display the PL spectra recorded on fresh solutions and curves 2 to 8 are the spectra after different storage time of 2, 6, 13, 43, 445, 647 and 697 days. Both figures reveal an important PL enhancement with some

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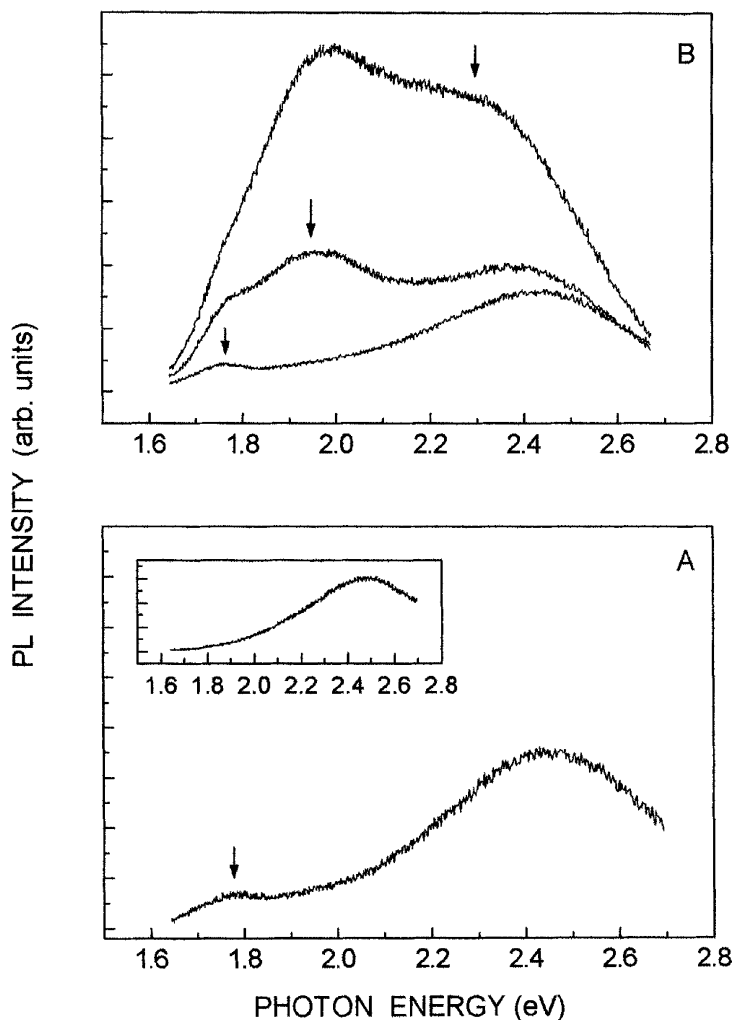
FIGURE 1 (A) PL spectrum of fresh prepared C_{60} solution in DCB with fullerene content of 0.4 mg/ml. In the inset it is shown the emission spectrum of DCB. (B) PL spectra of C_{60} solutions in binary solvent mixture NMP:DCB with a volume ratio of 1:5. From bottom to top are presented the curves recorded on fresh prepared solution and stored one and two years, respectively.

particularities depending on concentration. For the solution of higher concentration the enhancement of PL intensity is dominated by the increase of the red emission. On the contrary, the green emission prevails in PL spectra corresponding to the solution of lower concentration.
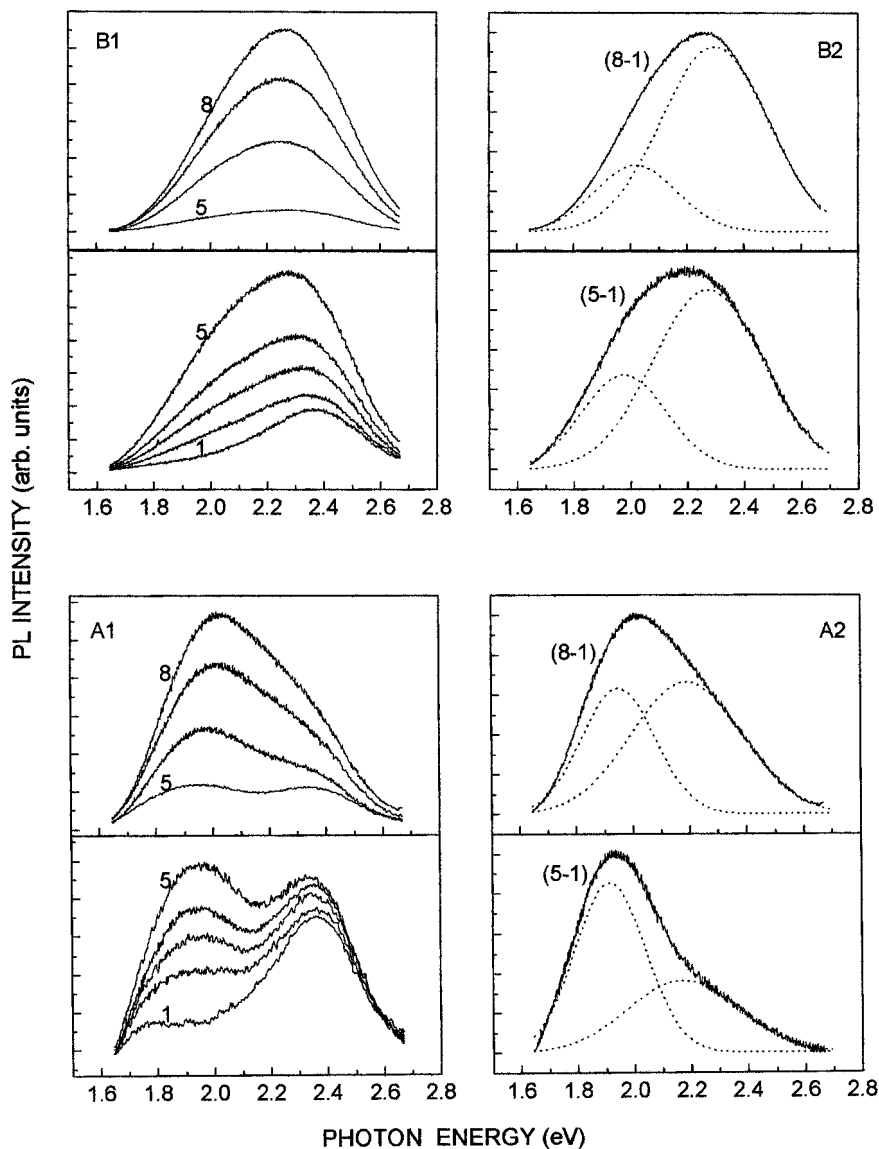
FIGURE 2 (A1 and B1) Variation of PL spectra with storage time for two C_{60} solutions in NMP of 2 and $0.5 \, \text{mg/ml}$ concentration, respectively. Curves 1 correspond to fresh prepared solutions. Curves 2 to 8 show PL emission after a storage time of 2, 6, 13, 43, 445, 647 and 697 days. (A2 and B2) Difference spectra (5-1) and (8-1) in a normalized scale. With dotted line the result of spectra fit with two Gauss functions is shown.

The data from Figure 2A1 and Figure 2B1 become more relevant if we eliminate the contribution of the solvent. That is achieved by the subtraction of the spectrum 1 from the other spectra. In a normalized scale the difference spectra for both solutions, between the curves 5 and 1 as well as between 8 and 1 are displayed in Figure 2A2 and Figure 2B2, respectively. The curves so obtained were fitted with two Gauss profiles (dotted lines) whose weight in the whole emission is seen to depend both of concentration and storage time. Fitted PL data show clearly that the increase of storage time results in a greater weight of the green emission, regardless of the concentration of solutions. However, the main conclusion that can be draw from these data, is that the PL enhancement practically begins with the red emission and ends always with the green. Although the two components increase simultaneously no connection was observed between their growths.

Similar results were obtained on thin films prepared by the solvent evaporation. In normalized scale Figure 3 shows a photoluminescence covering the same spectral range whose maximum shifts towards higher energy with decreasing of the fullerene concentration. PL curves presented here were recorded on films deriving from three aged solutions with C_{60} concentrations of 2, 1 and 0.5 mg/ml.
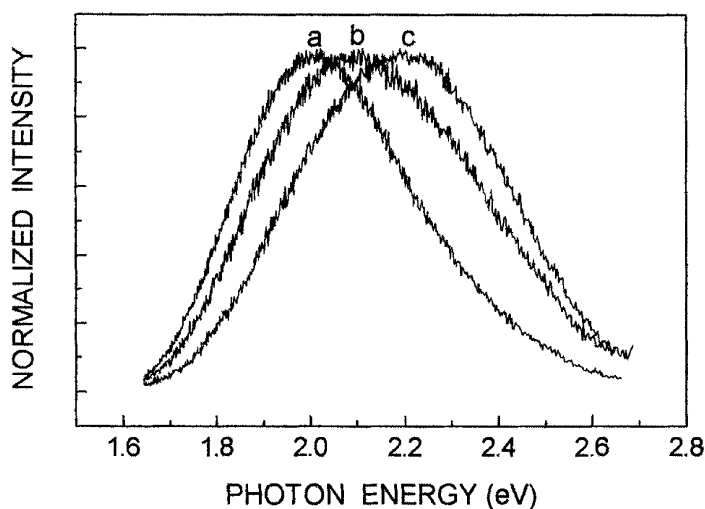
FIGURE 3 Normalized PL spectra of thin films prepared from three aged C_{60} solutions in NMP with fullerene content of 2, 1 and 0.5 mg/ml, curves a, b and c, respectively.

Convincing evidence that PL enhancement originates in two different processes, one faster responsible for the red emission and another one slower resulting in the increase of green component is brought by Figure 4A and Figure 4B. Thus, in Figure 4A the areas under PL curves of the more concentrated solution are plotted against the storage time.
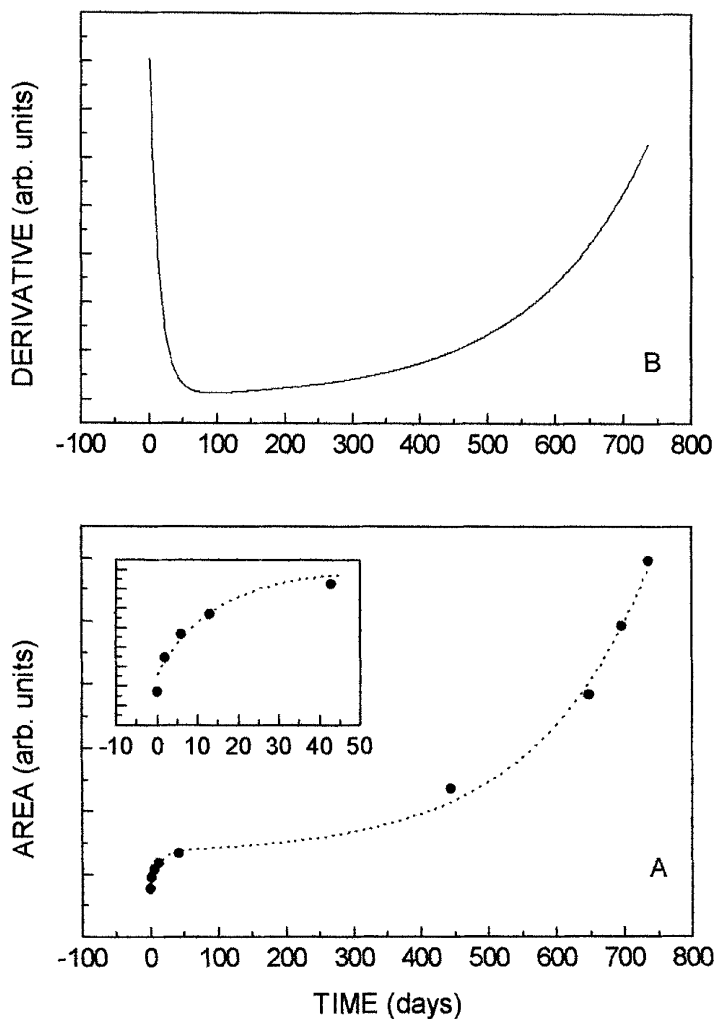
FIGURE 4 (A) Areas under PL curves 1 to 8, Figure 2A1 versus storage time. The fitting curve is plotted with dotted line. Shown in the inset is a "zoom" presentation of the first five experimental data. (B) Derivative of fit function against the storage time.

The fitting curve is shown in dotted line. Data were well fitted with a sum of exponential functions as follows:

$$A = A_0 + A_1(1 - \exp(-k_1 t)) + A_2 \exp(k_2 t) \qquad (1)$$

where A_0 is an offset parameter, A_1 and A_2 are the amplitude of the two exponential terms and k_1 and k_2 are assimilated with the rate constants met in the chemical reactions. The inset in Figure 4A presents the first five experimental data.

Based on the proportional relationship between areas and the number of luminescent centers formed in solution, the fit function (1) can be rightly considered as a rate equation written under its integral form. Two different regimes of PL generation rate are clearly put in evidence both in Figure 4A and especially in Figure 4B where the derivative of the function (1) is shown. In the shorter storage time domain, featured by the red emission development, the generation rate of luminescent entities decreases quickly. At longer storage time, where the green emission becomes the PL dominant component, the rate increases slowly following an exponential law. The particular shape of the rate curve in Figure 4B illustrates well not only a different kinetics for the red and green components but also the fact that the processes, where the two emissions originate from, take place in succession.

Any further explanation concerning the two successive processes must take into account that they are slow enough to be considered as chemical reactions, leading to the formation of new molecules. Therefore, we are tempted to regard them rather as molecular association processes, which preserve in the greatest part the molecular identity of C_{60} and NMP. In this perspective, the first process, running at shorter storage time could symbolically be described as:

$$C_{60} + NMP \rightarrow (C_{60}, NMP) \qquad (2)$$
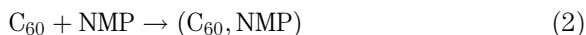
In terms of chemical kinetics, relation (2) pictures an apparently bimolecular process. However, considering that even the solvent is one of the reactants, the process is rather a pseudo-mono-molecular one, evidenced by the expression $A_1(1 - \exp(-k_1 t))$ from relation (1) that is typical for a kinetics of first order.

For the second process, the only alternative which we have is an aggregation of previous formed (C_{60}, NMP) entities. A priori, such a process develops in a nonlinearly manner, it appears as an avalanche-like phenomenon that fits well with the exponential increasing of luminescence at longer storage period of time, shown in Figure 4A. Anticipating, the aggregation is thought to be accomplished with the active participation of solvent molecules, which end up being incorporated in the newly born

molecular structures. Using again a symbolical writing, such aggregation process, mediated by solvent molecules may be depicted as:

$$(C_{60}, NMP) + (C_{60}, NMP) + NMP \rightarrow [(C_{60}, NMP), NMP, (C_{60}, NMP)] \quad (3)$$
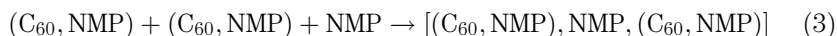
Returning at the relation (2) and cumulating the electrophilic character of C_{60} and the nucleophilic properties of NMP molecules, conferred by the electron lone pairs of nitrogen and oxygen, we can assimilate (C_{60},NMP) entities to molecular complexes of donor-acceptor type. For the time being we cannot specify the number of NMP molecules which are effectively attached to C_{60} cage. Interestingly, molecular complexes with four solvent molecules bound to the C_{60} cage were reported even when benzene and toluene have been used as solvents [15,16].

Supposing that PL emission of (C_{60},NMP) molecular complexes retains the main characteristics of the components modified to a certain extent, then the curve (5–1) from Figure 2A2 representing the PL enhancement measured after a shorter storage time can be explained as follows: the red band at about 1.92 eV is the blue shifted fluorescence of [C60] fullerene and the green band peaking around 2.18 eV is the red shifted fluorescence of NMP molecules.

Generally, the magnitude of the shift for absorption as well as an emission band depends on the strength of environmental intermolecular interactions. Passing from free [C60] fullerene as it exists in powder form to solvated C_{60} as in various aromatic solvents, the fluorescence band shifts from 1.68 eV to 1.77 eV. An additional blue shift of C_{60} emission is expected in NMP, where beside Van der Waals type forces encountered in commonly used fullerene solvents other stronger forces related to a donor-acceptor interaction are presented. Or, the position of the red emission, at about 1.92 eV is found in agreement with our expectations. Moreover, result of symmetry–lowering effects, the shift may be accompanied by important changes of the fluorescence yield. Regarding the green band, a greater red shift of the fluorescence originating in solvent molecules, reported at the value of 2.38 eV, means, in its turn, a stronger perturbation degree and vice versa.

The subsequent aggregation of (C_{60},NMP) entities, ending in more intricate molecular structures is highlighted in PL curves recorded at longer storage time by a dramatic increase of the green band weight (see curve (8-1), Figure 2A2). Considering the green component as the signature of perturbed NMP molecules, we can explain such enhancement only if we accept that in genesis of new structures not only (C_{60},NMP) entities, seen as bricks, but also a supplementary number of solvent molecules are involved. Now, the right member of Eq. (3) is quite understandable. It allows us to make a clear distinction between the solvent molecules as constitutive part

of molecular complexes and those included later. By analogy with some crystallization processes from aqueous solutions these additional solvent molecules become fixed in the aggregated structure as water molecules into crystalline structure. For C_{60} fullerenes a clathrate structure [18] is the most appropriate.

Careful analysis of the curves (8-1) from Figure 2A2 and Figure 2B2 reveals that in the case of less concentrated solution the green band occurs around 2.30 eV, closer to the fluorescent band of solvent molecules. Considering the red shift as a measure of the perturbation degree of the incorporated NMP molecules, we must accept that the aggregates formed at longer storage time in diluted solutions are not identical with those formed in concentrated solutions where the green band is found at about 2.22 eV.

There are two ways to explain this result. One by analogy with the crystallization from liquid phase: in solutions of higher concentrations a rapid crystallization occurs which leads to many and less perfect crystallites of smaller size, while in the less concentrated solutions the crystallization develops slowly forming larger and ordered three dimensional crystalline structures. Another way to explain proceeds from the hypothesis that the dipole moment of (C_{60},NMP) entities formed in concentrated and in diluted solution respectively is not the same. Idea is somehow sustained by recent electrooptical measurements [17], which put in evidence the generation, only in diluted solutions, of polar asymmetric C_{60} complexes with NMP molecules. In this scenario, a stronger dipolar character favours the insertion of more NMP molecules, which are also polar species, into the aggregated structures.

A plausible explanation for genesis of such different (C_{60},NMP) molecular complexes could be found out in the particularities of intermolecular interaction between [C60] fullerene and NMP. Thus, it is known that C_{60} is just a mild electron acceptor [10,11]. On the other hand, a presumable internal conjugation of lone pair electrons belonging to amine nitrogen, with the electrons of carbonyl group, (p-π conjugation), determines the NMP molecule, which is a substituted cyclic amide, to be a weaker donor of electrons. In these circumstances and considering also the general tendency of C_{60} to self-aggregate, the donor–acceptor interaction resulting in (C_{60},NMP) loose molecular complexes becomes very sensitive to the surrounding. More solvent molecules in the proximity of [C60] fullerene, as in diluted solutions, advantages evidently the progress of the charge transfer.

Another solvent, pyrrolidine (P), with a molecule containing only amine group, is a more efficient donor of electrons that favours the rapid formation of (C_{60},P) complexes. From the stronger interaction between C_{60} and P molecules results more polar (C_{60},P) complexes than (C_{60},NMP).

Difference has to be noticed also in PL spectra. Indeed, in Figure 5A and Figure 5B, one can see that PL spectra of the C_{60} solutions in P, recorded after 68 days of storage are very similar to each other, and are no more dependant of the fullerene concentration. Moreover, the analysis of PL curves from Figure 5 discloses also two components, a red and a green band, quite similar to those found in curve (5-1), Figure 2B2. From this result we conclude about the determinant role played by the lone pear electrons of the nitrogen heteroatom in the initiation of similar processes in the two nucleophilic solvents used, NMP and P.
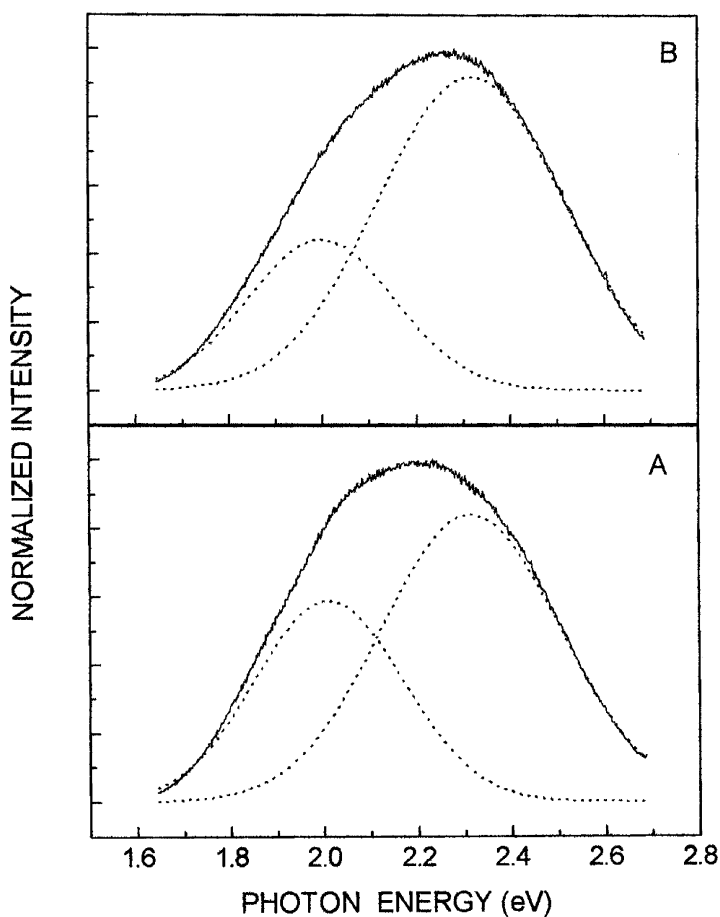
FIGURE 5 Normalized PL spectra of two C_{60} solutions in P with fullerene content of 2 and 0.5 mg/ml, A and B, respectively.

4. CONCLUDING REMARKS

Intermolecular interactions between [C60] fullerene and NMP solvent molecules are revealed in PL spectra by an emission whose intensity increases gradually with the storage time of solutions. Two emission bands, red and green, ranging at 1.92–2.00 eV and at 2.18–2.30 eV, respectively were identified. Their weight in the whole PL emission depends on the concentration of C_{60} and on the age of the solutions. Red emission is the dominant component in more concentrated solutions. The green emission prevails in diluted solutions and increases at longer storage time for all used concentrations.

PL data show that the two red and green emissions are the result of two successive processes, featured by different kinetics. The first process involved in the red emission generation is characterized by first-order kinetics. It is considered that this faster process is a charge transfer between [C60] fullerene as acceptor and NMP molecules as donor forming (C_{60},NMP) molecular complexes, which preserve in the greatest part the emission characteristics of the original molecules. The second process, resulting in an exponential enhancement of the green emission is consistent with a slow aggregation of previously formed (C_{60},NMP) molecular complexes. The process goes on with the active participation of solvent molecules, which end up being incorporated in the structure of newly born aggregates.

PL spectra of C_{60} solutions in P disclose the presence of the same two emissions, red and green. This result proves not only the similitude of luminescent processes that occur in the two nucleophilic solvents used, NMP and P, but especially the fact that these processes are triggered by the lone pear electrons of nitrogen heteroatom.

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