Interaction between poly(vinyl pyrrolidone) PVP and fullerene C₆₀ at the interface in PVP-C₆₀ nanofluids–A spectroscopic study

M Behera¹*, S Ram²

¹Chemistry department, Silicon Institute of Technology, Bhubaneswar-751 024, India
²Materials Science Centre, Indian Institute of Technology, Kharagpur-721 302, India

*Corresponding author Email: mano.silicon@gmail.com

Abstract. Fourier transform infrared and Raman bands shows a discernible enhancement in band intensity of C−H stretching, C=O stretching, C−N stretching, C−H₂ bending, and C−H₂ in-plane bending in PVP molecules in the presence of C₆₀ molecules. Amplification in intensity is ascribed to microscopic interactions results when a donation of nonbonding electron (n) occurs from a “=N−C=O” entity of PVP into a lowest unoccupied molecular orbital of the C₆₀ molecule in PVP-C₆₀ charge transfer (CT) complex. The C=O stretching band intensity (integrated) Vs C₆₀ content plot exhibits a peak near a critical 13.9 μM C₆₀ value owing to percolation effect. Light emission spectra show that even a small addition of 4.63 μM C₆₀ able to suppress the band intensity by ∼23% as a result of an energy loss. The integrated band intensity also decreases through a peak near 13.9 μM when plotted against the C₆₀-content. In correlation to the vibration spectra, the maximum effect observed both in light emission and excitation spectra suggests a percolation effect in the CT complex. Exhibition of percolation threshold in C₆₀-PVP donor-acceptor complex will be helpful in optimizing the photovoltaic properties vital for solar cell applications.

1. Introduction
Since inception, fullerene (C₆₀) – an allotrope of carbon has been attracting most to the research community around the globe owing to its distinctive physico-chemical properties. Spanning of electronic absorption bands in the large part of UV–Vis spectrum, excellent electron acceptor quality, low reorganization energy, and ability to generate efficient reactive oxygen species like singlet oxygen in solution make C₆₀ an attractive ingredient for various applications such as antibacterial activity, solar cells, photodynamic therapy, and photo-catalyst. Donor-acceptor systems where C₆₀ act as electron sink are of potential applications in molecular electro-active devices and work as model compounds for artificial photosynthesis. It is reported that the electron transfer from an organic compound to C₆₀ molecule via photo-irradiation is an essential requirement for designing of organic solar cells¹–³. In organic photo-voltaics, C₆₀ and derivatives act as acceptors due to their high electron accepting ability, high electron conductivity, and great potentiality to promote charge separation at the donor/acceptor interfaces [4–10]. The photo-conversion efficiency of solar cells can be improved in presence of C₆₀ cluster as they can minimize the direct interaction between the excited sensitizer and redox couple [4]. In recent years, work on polymer/C₆₀ bulk hetero-junction photovoltaic cells are bringing attention because of their potential inexpensive fabrication route, light weight and high rate of production [6,9]. C₆₀ based ultrathin layers are used in organic light emitting devices as a backlight for liquid crystal displays [7,8]. Presence of C₆₀ molecules leads to increase the photoconductivity of conducting polymers and organo-metallic compounds owing to photo-induced charge transfer processes useful for photovoltaic applications [5,10].
In spite of wide applications of C\textsubscript{60} based materials, the limited solubility and prone to aggregation in most aqueous \& non-aqueous solvent greatly hinders the progress in most of the proposed applications. In this regards, various methods have been proposed to improve the solubility and stability of C\textsubscript{60} in solution media. The development of C\textsubscript{60} dyad systems and their assembly via surface modification route is proved to be an excellent method as the C\textsubscript{60} moiety in such donor-acceptor systems almost retains its redox and various photo-physical properties. In this route, a stabilizing agent is added so that C\textsubscript{60} molecules can fully coated/encaged by a thin surface layer which facilitates solubilization/dispersion process in a solvent [11–20]. We have used poly(vinyl pyrrolidone) PVP as surface modifier to develop PVP-C\textsubscript{60} nanofluids (NFs) in n-butanol and water [11,19,20]. PVP polymer is a non-toxic biocompatible material with high complexing ability [11–20]. Also, PVP molecules has the ability under copolymerization reaction with poly(vinylidene fluoride), poly(vinyl alcohol), polyacrylonitrile, poly(vinyl chloride), and poly(vinyl formal) in many inorganic or organic solvents. It has been used extensively as a solubilizing agent and to form rheo-optical NFs. The lone pair of electrons present on O and N atoms of the pyrrolidone and ability to undergo keto-enol tautomerism helps PVP to solubilize C\textsubscript{60} molecules in water or in many non-aqueous solvent as they form donor-acceptor type complex [11,19,20].

There are lots of literatures available to support the existence of interfacial interaction between a donor and acceptor using vibration and photoluminescence (PL) spectroscopy. In a paper, Hartestein et al. [21] reported that C–H stretching band intensity is enhanced in 4-nitrobenzoic acid as largely as 10\textsuperscript{4} times when a thin silver over layer (0.2–6 nm) forms over it. As it is pointed out by Konarev et al., [22] a complex formation of C\textsubscript{60} with an organic electron donor gives rise to only a very small 1-2 cm\textsuperscript{-1} shift in some of the C\textsubscript{60} bands owing to an unfavorable steric effect. Shifting of C=O stretching frequency to the lower value by 60 cm\textsuperscript{-1} has been observed as a result of formation of a bond between >C=O group and Pt in a CT complex [23]. In another report, Xian et al. [24] have observed a size-dependent interaction of PVP with Pd NPs. For example, Pd NPs (~20 nm diameter) bond to PVP on both the O\textsuperscript{2-} and N\textsuperscript{3-} sites over >N–C=O moieties in pyrrolidone rings. Finer Pd NPs of diameter ~5 nm adsorb PVP merely on the O\textsuperscript{2-} sites. As much red-shift as 4 cm\textsuperscript{-1} has been observed in the C=O stretching frequency in a PVP–Pd complex when PVP monomer to Pd molar ratio (\(\varphi_{pm}\)) was taken to be 1.0. This value had been increased to as large as ~22 cm\textsuperscript{-1} on \(\varphi_{pm} \rightarrow 0.005\). As also reported by Grace and Pandian [25], only a weak coordinative chemical bonding appears via C=O moieties of PVP with a nanogold in this example of NFs, showing a marginally decreased C=O (PVP) stretching frequency by 10 cm\textsuperscript{-1}. Ramakanth and Patnaik [26] reported that C\textsubscript{60} quenches light–emission of pyrene by as much as 90 \% at 0.05 mM content. Sluch et al. [27] suggested that pyrene loses light emission intensity drastically to a low value in presence of C\textsubscript{60} molecule due to its high electron affinity.

In this paper we report a study on the vibrational and luminescence spectra of PVP-C\textsubscript{60} NFs in n-butanol. The vibrational properties of the synthesized NFs were studied to verify the existence of interaction between PVP and C\textsubscript{60} molecules using Fourier Transform Infrared (FTIR) and Raman spectroscopy. The photoluminescence (PL) properties were studied in terms of light emission and excitation spectra.

2. Experimental

2.1. Materials and method

We used C\textsubscript{60} powder (99.9\% purity) and PVP (K-25) which were procured from Alfa Aesar and Aldrich chemicals, respectively. The two analytical grade solvents which are used for developing NFs are Toluene and n-butanol. In order to develop NFs we first prepare two precursor solutions (PS) of optimized concentrations. We named those two solutions as PS-1 and PS-2. PS-1 solution has a C\textsubscript{60} concentration 1.39 mM and the PVP which was named as PS-2 has 1.1 M. As our aim was to prepare NFs of various concentrations, we added different volumes of PS-1 to five different batches of the PS-2 using syringe. The mixture solutions were stirred magnetically at room temperature. It was then sonicated at 50 °C for 20 min by fixing the frequency at
20 kHz and power at 250 W. Then we remove toxic toluene solvent by keeping them in a vacuum oven maintained at 3 kPa pressure and 110 °C for a period of ∼10 h. In this manner we obtained solid samples of PVP-coated C₆₀. As our motto was to develop NFs in an aqueous medium, we added deionized water to the solid PVP-surface modified samples of C₆₀ and then sonicated at 50 °C to develop aqueous C₆₀ NFs. We adopted a procedure to confirm the final C₆₀ concentration in our developed aqueous PVP solutions as described in literatures [11,19,20].

2.2. Characterizations

Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Corporation, Model NEXUS-870) was used to study the vibrational spectra of prepared nanofluids. Attenuated total reflectance mode was selected while recording the vibrational spectra. We used sample holder made of ZnSe crystal. Computer-assisted Perkin-Elmer (Model-LS 55) luminescence spectrometer was used to record emission and excitation spectra of samples. The instrument was fed with a red sensitive PMT detector (RS928) and a high-energy pulsed xenon discharge lamp was used as an excitation source (average power 7.3 W at 50 Hz). Raman spectrometer (Renishaw, 514 nm Argon ion laser, 40mW) was used to record Raman spectra of our samples.

3. Results and discussion

3.1. FTIR and Raman bands in PVP-C₆₀ NFs

We studied FTIR and Raman bands in illustrating the donor-acceptor type interaction between C₆₀ and PVP solubilized in n-butanol. Figure 1 shows typical FTIR bands in C₆₀-PVP NFs consisting of (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C₆₀ with 40.0 g/L PVP in n-butanol. As expected, an increase in the C₆₀ dosage clearly appears in selective IR bands either in their frequencies or peak intensities. The band intensity is enhanced markedly in the C−H stretching bands shown at 2963, 2935, and 2874 cm⁻¹, C=O stretching band at 1666 cm⁻¹, two C–N stretching bands at 1497 and 1291 cm⁻¹, C–H₂ bending at 1463, 1438, and 1321 cm⁻¹, and C–H in-plane bending at 1223 and 1378 cm⁻¹ in PVP molecules in the presence of C₆₀ molecules. Such features of microscopic interfacial interactions arise in a PVP-C₆₀ nanofluid when a donation of lone pairs of electron occurs from a “>N–C=O” moiety into a LUMO (t₁u) band of the C₆₀ molecule in a CT complex [16–18].

Figure 1. (A) FTIR spectra of C₆₀:PVP NFs with: (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C₆₀ with 40.0 g/L PVP in n-butanol; (B) Variation of C=O stretching band intensity (integrated) with the C₆₀ contents.
Furthermore, the 1665 cm\(^{-1}\) C=O stretching band of parent PVP is decreased progressively to 1659 cm\(^{-1}\) upon loading-up C\(_{60}\) up to 13.9 μM with a markedly enhanced peak intensity in a spectrum in figure 1d. As plotted in Fig. 1B, this band exhibits a peak in its integrated peak intensity at this critical 13.9 μM C\(_{60}\) value owing to a percolation effect. It is a result of a weak interfacial interaction of PVP with the C\(_{60}\) molecules in the NFs [11,19,20,23–25]. The various FTIR and Raman bands observed in a bare sample 40 g/L PVP in \(n\)-butanol and that modified with a selective 18.52 μM C\(_{60}\) dosage in the form of a nanofluid are given in Table-1. In a close correlation with the various literatures’ results on reinforced PVP using different kinds of metal particles [23–25,28,29], our studies of the synthesized PVP-C\(_{60}\) NFs explicitly reveal that the PVP molecules are bonding over a nascent C\(_{60}\) nanosurface only weakly through the “>N–C=O” moieties (PVP) owing to primarily of steric restrictions.

Table-1 FTIR and Raman bands observed in 40.0 g/L PVP and that containing 18.52 μM C\(_{60}\) in \(n\)-butanol of NFs.

| FTIR band (cm\(^{-1}\)) | Raman Band (cm\(^{-1}\)) | Assignment [23-25,28,29] |
|-------------------------|-------------------------|--------------------------|
| PVP                     | C\(_{60}\)-PVP           |                          |
| 2963                    | 2961                    | C-H stretching           |
| 2935                    | 2933                    | C-H stretching           |
| 2874                    | 2870                    | C-H stretching           |
| 1666                    | 1659                    | C=O stretching           |
| 1497                    | 1494                    | C-N stretching           |
| 1463                    | 1461                    | C-N stretching           |
| -                       | -                       | 1447                    | C-N stretching           |
| 1438                    | 1436                    | 1425                    | C-N stretching           |
| 1378                    | 1376                    | 1373                    | C-H in-plane bending    |
| 1321                    | 1318                    | 1312                    | C-H\(_2\) wagging        |
| 1291                    | 1288                    | -                       | C-N stretching           |
| 1223                    | 1221                    | 1230                    | C-H in-plane bending    |

Figure 2 (a-f) compares Raman spectra for the PVP-C\(_{60}\) NFs which contain varied dosages of C\(_{60}\) from 0 to 18.52 μM along with a common 40 g/L PVP value of a surface modifier. Like the IR spectra in figure 1, the C\(_{60}\) addition exhibits a marked change in the selective band. Raman bands in the local vibrations in the PVP molecules. The surface enhancement Raman scattering is clearly shown in the C=O stretching band of 1659 cm\(^{-1}\), in the C–N and C=C stretching of 1499, 1465, 1447, and 1,425 cm\(^{-1}\), in the C–H in-plane bending of 1373 and 1230 cm\(^{-1}\), and in the C–H\(_2\) wagging of 1312 cm\(^{-1}\) in the pyrrolidone ring of PVP molecules in the presence of C\(_{60}\) exfoliated molecules which extend a CT interaction with the PVP. Eventually, both the C=O and C–N sites from localized >N–C=O moieties in PVP molecules perceive an
interface interaction with the C$_{60}$ molecules as it is reflected in a small red-shift of 5-8 cm$^{-1}$ in the respective bond stretching frequencies besides effectively enhanced band intensities. Small Raman shift characterizes only a weak CT interaction taking place between the two PVP and C$_{60}$ entities which appear in presumably small joint assemblies. Further, we studied the integrated Raman band intensity (I$_{int}$) for the C=O stretching vibration in PVP in the PVP-C$_{60}$ NFs in n-butanol. A plot made in Fig. 3 reveals that the I$_{int}$ exhibits a peak near a C$_{p1}$ = 13.2 μM C$_{60}$ value, which compares well to a value 13.9 μM C$_{60}$ found from the IR bands.

![Raman bands of C$_{60}$:PVP NFs consisting of (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C$_{60}$ with 40.0 g/L PVP in n-butanol, with (B) a variation of C=O stretching band intensity (integrated) with the C$_{60}$ dosages.](image)

**Figure 2.** Raman bands of C$_{60}$:PVP NFs consisting of (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C$_{60}$ with 40.0 g/L PVP in n-butanol, with (B) a variation of C=O stretching band intensity (integrated) with the C$_{60}$ dosages.

### 3.2. Emission and excitation spectra in PVP-C$_{60}$ NFs

Now let us analyze light emission spectra observed in the PVP-C$_{60}$ NFs which contain (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C$_{60}$ along with 40.0 g/L PVP in n-butanol. Figure 3 compares the spectra measured over 350-550 nm by exciting the samples at a common λ$_{em}$ = 325 nm in order to comment on the effects of the variation of the C$_{60}$ dosages on the emission bands. A virgin sample before adding any C$_{60}$ exhibits a strong light emission with λ$_{max}$ lying at 395 nm in bare PVP polymer dispersed in n-butanol. This band refers to the n ← nπ* transition from C=O moieties in exfoliated PVP configurations as it is also observed earlier in PVP solution [19,20,29–33]. Even a small addition of only 4.63 μM C$_{60}$ suppresses this band significantly so as it appears in a broad band (Band-1) which is red-shift to 401 nm with a nearly ~23% decreased peak intensity. This is a result of an energy loss of the light-emission which confers an n-electron transfer from pyrrolidone group to the electron deficient C$_{60}$ in a PVP-C$_{60}$ CT complex. As large as ~67% fall in the emission intensity of bare PVP polymer occurs in this region when the C$_{60}$ dosage is increased to 18.52 μM C$_{60}$ in a sample of 40.0 g/L PVP in n-butanol.

As shown in the inset of figure 3, a deconvolution of light emission spectrum in the virgin PVP describes two overlapping bands of λ$_{max}$ lying at 400 and 435 nm. The band at 435 nm (Band-2) occurs from the n ← nπ* transition from >N–C moieties in exfoliated PVP configurations. We also studied normalized emission band intensity (I$_{em}$) in the two bands over the 0–18.52 μM C$_{60}$-contents. As portrayed in figure 4, the I$_{em}$-value falls down with C$_{60}$-content showing a small plateau over 8–14 μM C$_{60}$ before it drops rather rapidly when the localized electron density has decreased over the C$_{60}$ surfaces.
Figure 3. Light-emission in C$_{60}$:PVP NFs having (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C$_{60}$ along with 40.0 g/L PVP in n-butanol, with a deconvolution of spectrum (c) in two overlapping bands is the inset as per the energy level diagram in the right.

To analyze whether the light-emission in PVP-C$_{60}$ NFs follows the excitation process from the energy levels of the same optical species in a sample, we studied the excitation spectra by irradiating the samples in the emission band under identical conditions. Figure 5 shows the results of the excitation spectra which were scanned by irradiating the different samples at a common emission wavelength $\lambda_{\text{em}} = 400$ nm. As expected, also the excitation spectrum loses its intensity over 290–420 nm on the presence C$_{60}$ of different dosages from 4.63 to 18.52 μM in a 40.0 g/L PVP in n-butanol.

Figure 4. The intensity in emission bands (integrated value) plotted against C$_{60}$-content in C$_{60}$:PVP NFs in n-butanol, with electron density varied over C$_{60}$ surfaces in three regions of the plot.

Both the emission and excitation spectra follow the same trend of the intensity loss as a function of the C$_{60}$ content. These results confer unambiguously that the light emission and excitation spectra arise from the same optical entities of energy levels in the two regions. The spectra shown in figure 5A comprise at least three distinct bands overlapping on another. For example, a deconvolution of a typical spectrum (c) exhibits the three distinct bands of 334, 355, and 386 nm of the peak-values. The integrated band intensity ($I_{\text{ex}}$) also in the excitation spectrum decreases through a peak near $C_{p1} = 13.9$ μM when plotted against the C$_{60}$-content (Figure 5B). The results confer a correlation in the light absorption, emission and excitation spectra in the present PVP-C$_{60}$ NFs which all show a maximum effect at a common C$_{60}$ content of ~13.9 μM (a percolation threshold).
Figure 5. (A) Excitation spectra of C₆₀:PVP NFs having (a) 0, (b) 4.63, (c) 9.26, (d) 13.9, and (e) 18.52 μM C₆₀ with 40.0 g/L PVP in n-butanol, with a deconvolution of band (c) in three bands in the inset. (B) The C₆₀ doping induced intensity loss (integrated) over 290–420 nm.

4. Conclusion

The surface interaction between C₆₀ nanoparticle and PVP molecule in PVP-C₆₀ NFs was studied with the help of vibration and PL spectra. Amplification in the intensity some of the vibration band of PVP molecules in the presence of C₆₀ molecules is ascribed to an interfacial interaction which arise when a donation lone pairs of electron occurs from a “>N–C=O” moiety of PVP into the C₆₀ molecule in a CT PVP-C₆₀ complex. Red-shift in the emission band of PVP molecule in presence of C₆₀ molecule occurs as a result of an energy loss due to CT from PVP to C₆₀ molecule. Demonstration of percolation effect in the vibration property is well agreed with PL result in NFs. Existence of donor-acceptor interaction in a hybrid system is useful of photovoltaic applications.

References
1. Mishra A and Bauerle P 2012 Angew. Chem. Int. Ed. 51 2020
2. Ponseca C S, Nemec H, Vukmirovich, Fusco S, Wang E, Andersson M R., Chabera P, Yartsev A, and Sundstrom V 2012 J. Chem. Phys. Lett. 3 2442
3. Bartynski A N, Trinh C, Panda A, Bergemann, K, Lassiter B E, Zimmerman J D, Forrest S R, and Thompson M E 2013 Nano Lett. 13 3315
4. Kamat P V, Hara M, and Hotchandani S 2004 J. Phys. Chem. B 108 5166
5. Davidenko N A, Studzinski S L, Karapetyan A N, Ishchenko A A, Derevyanko N A, Spitsyna N G and Lobach A S 2007 J. Opt. Technol. 74 679
6. Cates N C, Gysel R, Beiley Z, Miller C E, Toney M F, Heeney M, McCulloch I and McGehee M D 2009 Nano Lett. 9 4153
7. Lv Z, Deng Z, Xu D, Li X and Jia Y 2009 Displays 30 23
8. Ryu S Y, Lee C H, Oh S, Song S Y, Hwang K H, Hwang H S, Han M H, Hwang B H, and Koo H 2010 Electrochem. Solid State Lett. 13 143
9. Brabec C J, Gowrisanker S, Halls J M, Laird D, Jia S and Williams S P 2010 Adv. Mater. 22 3839
10. Lin Y, Li Y and Lin X Z 2012 Chem. Soc. Rev. 41 4245
11. Behera M and Ram S 2012 J. Incl. Phenom. Macrocycl. Chem. 72 233
12. Popov V A, Tyunin M A, Zaitseva O B, Karaev R H, Sirotinkin N V, Dumpis M A and Piotrovsky L B 2008 Fuller. Nanotub. Car. N. 16 693
13. Ramakanth I and Patnaik A 2008 Carbon 46 692
14. Krasnou I, Tarabukina E, Melenevskaya E, Fillipov A, Aseyev V, Hietala, S and Tenhu H 2008 J. Macromol. Sci. B 47 500
15. Tong J, Zimmerman M C, Li S, Yi X, Luxenhofer R, Jordan R, and Kabanov A V 2011 Biomaterials 32 3654
16. Torres V M, Posa M, Srdjenovic B, and Simplicio A 2011 Colloids Surf. B: Biointerfaces 82 46
17. Liu S, Sui Y, Guo K, Yin Z, and Gao X 2012 Nanoscale Res. Lett. 7 433
18. Oriana S, Aroua S, Söllner J O B, Ma X –J, Iwamoto Y and Yamakoshi Y 2013 Chem. Comm. 49 9302
19. Behera M and Ram S 2015 Fuller. Nanotub. Car. N. 23 906
20. Behera M and Ram S 2015 Fuller. Nanotub. Car. N. 23 1064
21. Hartstein A, Kirtley J R, Tsang J C 1980 Phys. Rev. Lett. 45 201
22. Konarev, D. V., Semkin, V. N., Graja, A., and Lyubovskaya, R. N. (1998), Journal of Molecular Structure, Vol. 450, No. (1-3), pp. 11–22.
23. Borodko Y, Habas S E, Koebel M, Yang P, Frei H, and Somorjai G A 2006 J. Phys. Chem. B 110 23052
24. Xian J, Hua Q, Jiang Z, Ma Y, and Huang W 2012 Langmuir 28 6736
25. Grace A N and Pandian K 2006 Colloids Surf. A 290 138
26. Ramakanth I and Patnaik A 2008 Carbon 46 692
27. Sluch M I, Samuel I D W, and Petty M C 1997 Chem. Phys. Lett. 280 315
28. Mishra A and Ram S 2007 J. Chem. Phys. 126 084902
29. Mishra A and Ram S 2009 J. Phys. Chem. A 113 14067
30. Ram S and Fecht H J 2011 J. Phys. Chem. C 115 7817
31. Behera M and Ram S 2013 Appl. Nanosci. 3 543
32. Behera M and Ram S 2013 Int. Nano Lett. 3 17
33. Behera M 2015 Res. J. Nanosci. Nanotechnol. 5 60.

Acknowledgement

We acknowledge the support from Silicon Institute of Technology, Bhubaneswar, India in carrying out this work.