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Photoluminescence in fullerene-doped porous glasses

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Abstract. We report enhanced and broad-band photoluminescence (PL) behavior of C_{60} doped in porous silica glasses. By carrying out photoluminescence and photoluminescence-excitation spectroscopy of C_{60} doped in surface-unpassivated and -passivated porous glasses, we show that the interaction of C_{60} with the silica surface is quite strong and that the modified C_{60} molecules contribute only in the orange-red region (~ 1.9 eV) of the observed PL spectrum. The PL intensity in the blue-green region (~ 2.3 eV) observed in doped glasses is found to originate in the porous glass itself.

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Optical properties of fullerene-based composite materials are currently being investigated for their possible uses in various opto-electronic devices such as optical limiters [1–3]. Polymers and glasses provide an excellent medium for making composite materials due to their chemical inertness, mechanical stability and high transparency in the visible range. Porous media like porous silica glasses and zeolites with nanometer-sized pore diameter also provide a medium for making composites. These porous materials also provide us with an opportunity to study the effect of confinement on the physical and optical properties of confined molecules. When a molecule is confined within narrow pores with pore widths of few molecular diameters, the molecule is likely to behave differently and a range of new and unusual physical behaviors is exhibited [4]. One such behavior is the enhancement of broad-band visible photoluminescence (PL) from the C_{60}-doped porous media, like sol–gel-derived porous silica glass [5], zeolites [6, 7], porous silicon [8] and other porous metal oxides [9, 10]. C_{60} in other solid forms (thin films and single crystals) exhibits a weak photoluminescence in the near-IR range (~ 750 nm) [11, 12]. Observed blue shifts of PL emission from C_{60} in porous media like silica glass and zeolites were earlier attributed to effects like quantum confinement of C_{60} nanocrystals in the narrow pores, which results in widening of the HOMO–LUMO (highest-occupied-molecular-orbital to lowest-unoccupied-molecular-orbital) gap of the C_{60} solids [5]. For C_{60} doped in other porous metal oxides, the model of the oxidation of C_{60} upon interaction with the pore surface was proposed [10]. To understand the origin of enhanced and blue-shifted PL emission from C_{60} doped in porous solids, a systematic study of the PL emission is much needed. In this paper, we present our studies of photoluminescence and photoluminescence excitation (PLE) in C_{60}-doped Vycor porous glasses (PGs). We observe excitation-wavelength dependence of the PL spectra of undoped PG and C_{60}-doped PG, suggesting that the PG surface has many different radiative centers, which are selectively activated by different wavelengths. From PL and PLE spectroscopy on C_{60} doped in surface-unpassivated and -passivated porous glasses, we conclude that C_{60} interacts with the glass surface and this interaction modifies the guest as well as the host. The modified C_{60} molecules emit only in the orange-red region (~ 1.9 eV). The PL emission in the range higher than 1.9 eV, i.e. the blue-green range, is mainly due to the porous glass itself. Our study provides evidence for the model of C_{60} modification upon interaction with the pore surface.

We used Vycor-brand Corning 7930 porous silica glasses [13] for our studies. These glasses are characterized by a narrow pore-size distribution with average pore diameter ~ 4 nm and porosity $\sim 28\%$. The multiply connected nature of the pore geometry makes such material an amorphous-like system, creating an inhomogeneous distribution of adsorbed molecules. Moreover, chemical heterogeneity on the surface of the pores further modifies the photophysical property of the adsorbed molecules.

The as-received porous silica glasses were light yellow in color due to the adsorbed organic contaminants. The glasses were first cut into about $10\,\mathrm{mm} \times 10\,\mathrm{mm} \times 2\,\mathrm{mm}$ rectangular pieces and heated in air to $\sim 500\,°\mathrm{C}$. The heating was continued until all the contaminants were decomposed into CO_2 and other gaseous products and the glasses appeared clean and discolored. The glasses were allowed to cool in air and kept in a desiccator until use. A cleaned glass piece was dipped in a toluene solution of C_{60} for about 24 h and then subsequently dried at $\sim 100\,°\mathrm{C}$ to remove the

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toluene solvent. The glasses were then vacuum-dried to remove the solvent. Due to the porous nature and the inhomogeneity present in porous glasses, scattering losses in porous glass is a known phenomenon [14]. To reduce the scattering losses, we filled the remaining pore volume with the polymer polymethyl methacrylate (PMMA). For PMMA impregnation the monomer methyl methacrylate (MMA) was polymerized in situ [15]. The vacuum-dried C_{60} adsorbed glasses were immersed in a 0.125% benzoyl peroxide/MMA solution and kept overnight in a sealed container to let the solution penetrate into the glass. The container was kept at ~ 60 °C for about two days for complete polymerization of MMA. The completely polymerized PMMA-filled C_{60}-doped porous glasses were then removed from the container and polished to obtain transparent yellowish-brown-colored C_{60}-doped porous glasses.

For recording PLE and wavelength-dependent PL spectra we used a spectrofluorimeter (Spex-DM 300F) equipped with a tungsten–halogen lamp as a source of excitation. The PL spectrum was excited using 457.9-nm excitation of an argon-ion laser and was recorded using a Raman spectrometer U1000 (Jobin–Yvon) and detected using a R649 photomultiplier tube (PMT) in a photon-counting mode. This spectrum was corrected for the PMT response. All PL and PLE measurements were carried out at room temperature.

Figure 1a shows the absorption spectrum of C_{60} doped in unpassivated porous glasses. The absorption spectrum of C_{60} doped in unpassivated PG shows an almost continuously rising absorption from the near-IR range to the UV range. The spectrum is observed to be featureless as compared to the spectrum of C_{60} in solution [16]. The change in the absorption spectrum of C_{60} upon doping in porous glasses has been reported by us [17]. The PL spectrum of C_{60} in unpassivated PG is shown in Fig. 2 as a function of excitation wavelength. We observe that: (1) the PL spectrum is excitation-wavelength dependent, (2) the emission peak wavelength increases linearly with increase of excitation wavelength and (3) the PL spectrum is very broad-band. These PL features are quite similar to those normally observed in disordered solids like hydrogenated amorphous carbon or silicon [18]. It is also to be noted that similar features were observed for unpassivated pure PG also. These features imply that C_{60} molecules are adsorbed on an inhomogeneous and chemically heterogeneous surface of porous glass. Therefore the PL emission in C_{60}-doped unpassivated PG seems to have a multicomponent character with many radiative centers having their characteristic absorption and PL features. Such an inhomogeneous distribution of molecules adsorbed on a porous silica surface has been reported for several other organic dyes [19].

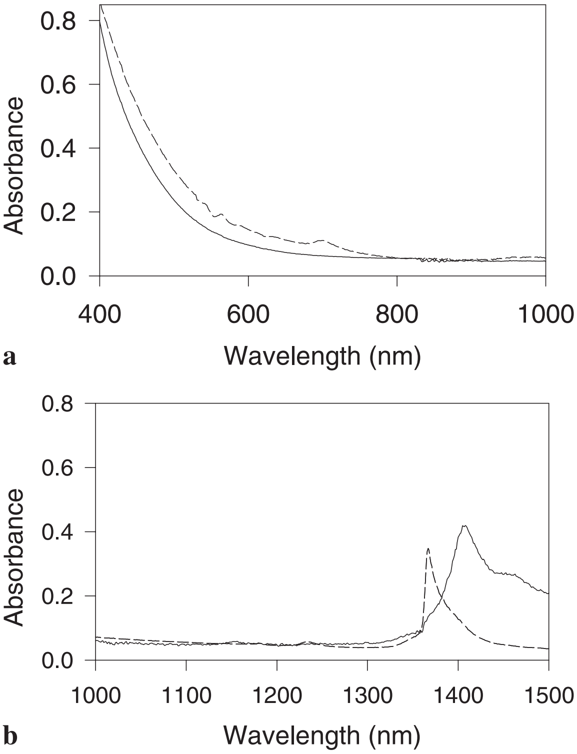

Fig. 1. a Absorption spectrum of C_{60} doped in unpassivated (*solid line*) and passivated (*dashed line*) porous silica glass. Pores of the glasses were filled with PMMA. **b** Absorption spectrum of undoped porous glasses in the IR range with and without surface passivation. The glasses were vacuum dried and without PMMA in the pores

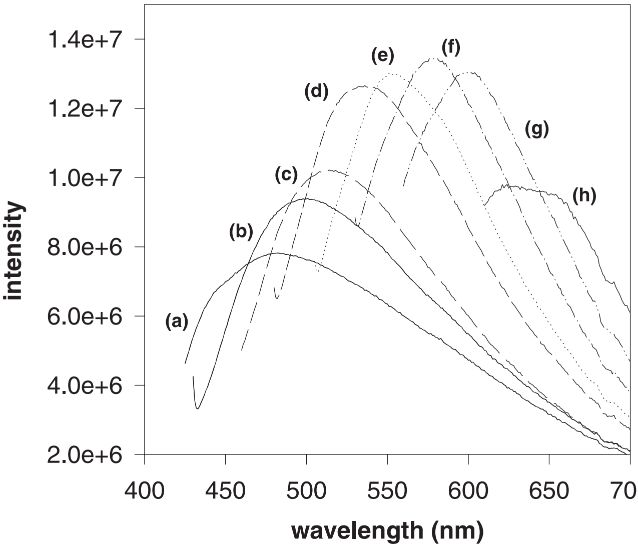

Fig. 2. Photoluminescence spectrum of C_{60} doped in unpassivated porous glass as a function of excitation wavelength. The excitation wavelengths were (a) 400 nm, (b) 425 nm, (c) 450 nm, (d) 475 nm, (e) 500 nm, (f) 525 nm, (g) 550 nm and (h) 600 nm

The PL intensity from undoped unpassivated PG was observed to be ~ 30 times weaker than C_{60}-doped PGs. We observe some similarities and differences in the two spectra as shown in Fig. 3. The spectrum of C_{60}-doped unpassivated PG (Fig. 3b) is observed to be asymmetric compared to the undoped one (Fig. 3a), with some additional intensity in the red region (550–700 nm). The enhancement of overall PL efficiency and the broadening of the PL spectrum can be attributed to the effect of doping of C_{60} in porous glass. In contrast to this, the PL emission in the blue-green range of unpassivated pure PG and in the doped one looks similar in line shape except for a slight blue shift and narrowing of the peak.

The porous oxides like SiO_2, TiO_2, Al_2O_3 etc. are known to fluoresce in the blue-green region [20]. The origin of PL in porous metal oxides has been shown to be due to structural defects present at the pore surface. The chemistry of the porous silica surface has been studied in detail and it is reported that the surface of the porous silica is covered with

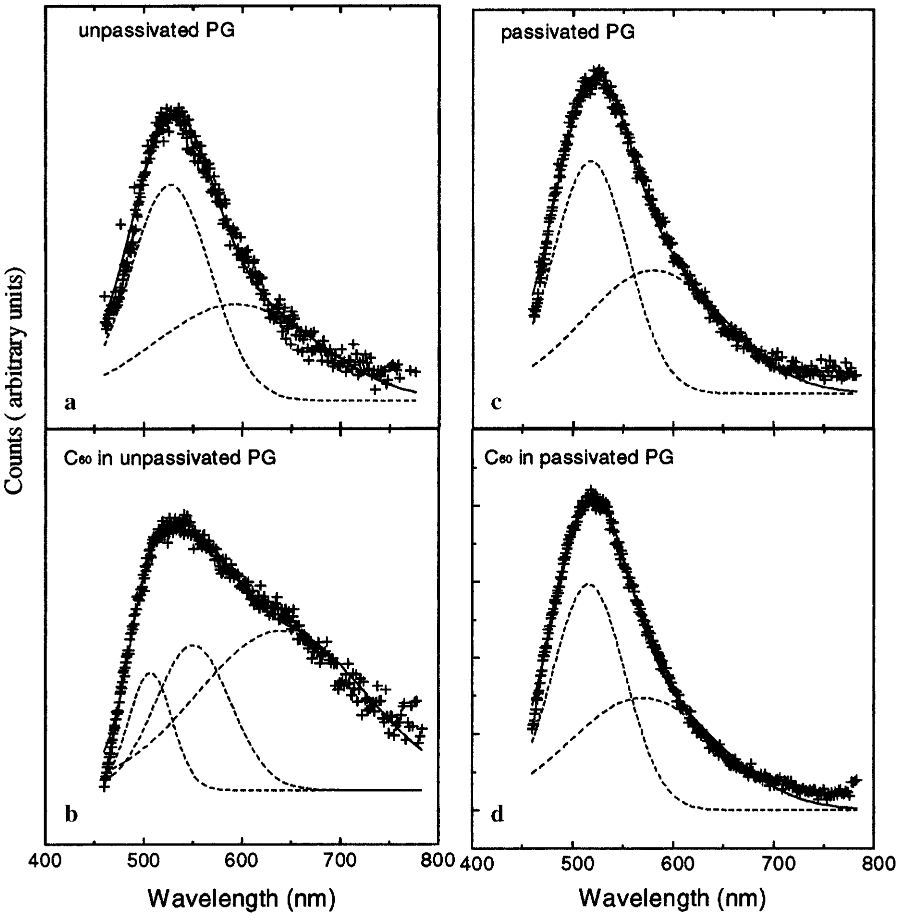

Fig. 3a–d. Photoluminescence spectra of undoped and C_{60}-doped porous glasses excited with 457.9-nm argon-laser line. **a** Unpassivated undoped porous glass, **b** C_{60} in unpassivated porous glass, **c** passivated undoped porous glass and **d** C_{60} in passivated porous glass. *Dashed curves* in each spectrum show the Gaussian fitting of the observed spectrum

silanol (–Si–OH) groups at the structural defect sites [21]. The intensity of PL emission in these glasses depends on the density of such defects, which in turn depends on the various methods of porous-glass preparation and the cleaning procedures adopted prior to doping of molecules in the pores. The broad-band PL emission from C_{60} doped in PG was similar to the PL emission observed by others, e.g. C_{60} in a sol–gel-derived silica aerogel [5], in zeolites [6, 7] and other porous metal oxides [9, 10]. The enhancement of about ∼ 30 times in the PL efficiency from the undoped porous glass to C_{60}-doped porous glass can be due to the nature of the interaction at the interface of C_{60} and the porous silica surface. Recently, Anpo et al. [22] have carried out a detailed investigation using ESR (Electron Spin Resonance), FT-IR and other spectroscopic techniques to understand the interaction of C_{60} dispersed in silica gel. They have shown that the interaction of C_{60} with the SiO_2 surface is quite strong and as a result C_{60} radicals are formed. Further, in the presence of O_2, stable suboxides of C_{60} ($C_{60}O_x$) are formed. We believe that a similar reaction is taking place at the interface of C_{60} and the silica pore surface. The formation of C_{60} radicals and their suboxides not only modifies the structure of C_{60} but also modifies the host surface. As a result, doping of C_{60} into the pores of silica modifies both the guest and the host. Therefore, on the surface of host porous silica there can be a further increase in the defect density. This may be the cause of the increase in the PL efficiency of porous silica in the blue-green range.

The enhancement of the PL intensity in the orange-red region in C_{60}-doped unpassivated PG can be due to the modified C_{60}. Due to the highly symmetric structure of C_{60}, the HOMO–LUMO transition $t_{1u} - h_u$ is a dipole-forbidden transition [23]. As a result of strong interaction of C_{60} with the silica surface, the symmetry of the C_{60} molecule gets lowered and the HOMO–LUMO transition becomes dipole-allowed. Thus a radiative de-excitation around ~ 1.9 eV, corresponding to the HOMO–LUMO transition in a C_{60} molecule, is observed in C_{60}-doped PG. The enhancement of luminescence from an epoxide of type $C_{60}O$, formed as a result of the interaction of oxygen or silanol groups with C_{60}, has been reported by several others [12, 24]. Andong et al. [24] reported that as a result of epoxide formation, the symmetry of C_{60} is reduced from I_h to C_{2v}, which causes a strong Jahn–Teller distortion and removes the degeneracy of the t_{1u} level. Therefore, the selection rule will change to some extent and dipole transitions among $h_u - t_{1u}$ can take place.

To confirm that the origin of luminescence in the red and blue regions is indeed from C_{60} and PG respectively and to understand the role of chemical groups present at the surface of the porous silica, we prepared a second set of samples of C_{60}-doped porous glasses. In the first case discussed earlier, the C_{60} is doped in porous glass without any pretreatment of the pore surface, while in the second set the surface of the pores was passivated by a chemical treatment and then doping of C_{60} was carried out, since as mentioned above the intensity of the PL emission in these glasses depends on the various methods of porous-glass preparation and the cleaning procedures adopted prior to doping of molecules in the pores. In the second set of samples, the cleaned porous glass was boiled in

1-propanol solvent for about 24 h. It is known that this process passivates the surface sites by derivatizing the silanol groups by 1-propanol. The reaction that takes place is [25]

$$\equiv \mathrm{Si{-}OH} + \mathrm{CH_3CH_2CH_2OH} \xrightarrow{\Delta} \equiv \mathrm{Si{-}OCH_2CH_2CH_3} + \mathrm{H_2O}$$

The derivatized glass samples were then dried at 100 °C in vacuum and cooled in a flowing argon gas atmosphere. The glasses were immediately dipped in the toluene solution of C_{60}. The adsorption of C_{60} in the pores of passivated PG was observed to be much slower than that in unpassivated PG. We had to keep the passivated PG immersed in C_{60} solution for about three days until some coloration due to C_{60} became visible. This was followed by PMMA infiltration as described earlier for unpassivated PGs.

The absorption spectrum of C_{60} doped in passivated PG (Fig. 1a) is observed to have some structure in the visible range. The observed structured spectrum resembles the spectrum of C_{60} in solution [16]. This suggests that there is a molecular dispersion of C_{60} molecules on the passivated PG surface with weak interaction of C_{60} at the surface. The absorption spectra of undoped PGs with and without surface passivation were observed to be similar in the visible-wavelength range, while a difference in the two undoped PGs, as shown in Fig. 1b, appears in the IR range (1000–1500 nm). It is known that in unpassivated PG the surface of the PG is covered with adsorbed water molecules and silanol groups. These surface-adsorbed species absorb strongly in the range ∼ 1410 nm due to the overtone absorption of an −OH group [26]. The spectrum of passivated PG exhibits a strong absorption in the range ∼ 1370 nm. The reaction of alcohols with the various chemical species at the porous glass surface is well studied [27]. It is reported that the passivation process not only forms a compound of the type Si–OR but also coordinated unsaturated centers of boron [27]. Such compounds may absorb in the higher energy than the Si–OH-type groups [28]. This indicates that the surface of the porous glass is passivated by 1-propanol treatment.

The PL spectrum of undoped and C_{60}-doped surface-passivated PG is shown in Fig. 3c and d. We observe that the two spectra are quite similar in spectral shape and position. In other words the effect of doping of C_{60} in the pores of surface-passivated PG does not seems to modify the guest molecules, while the presence of C_{60} in the pores of surface-passivated PG is confirmed by its absorption spectrum (dashed curve in Fig. 1a). The observed structures in the absorption spectrum of C_{60} doped in passivated PG are quite similar as observed for C_{60} in solution. It has been reported that the esterification process of passivation of PG with 1-propanol produces a spatially homogenous surface [29]. This implies that molecules of C_{60} are adsorbed on a spatially homogeneous passivated silica surface of the PG and there is no strong interaction of C_{60} molecules with the chemically active surface groups like silanols, which modifies C_{60}. This is also consistent with the observation that doping of C_{60} in passivated PG is more difficult and takes a longer time than in unpassivated PG.

To confirm the nature of the interaction of C_{60} adsorbed on unpassivated and passivated silica surfaces, PLE spectroscopy was used. We recorded a PLE spectrum in the range 400 to 650 nm of both the doped glasses by monitoring the PL intensity at 500 nm and 650 nm. The value of 500 nm was chosen to gain information on the origin of PL from pure PG and, since C_{60}-doped PG shows additional PL in the red region ∼ 650 nm, 650 nm was chosen to confirm its origin due to C_{60}. The PLE spectrum of C_{60} doped in passivated and unpassivated PG is shown in Fig. 4a and b respectively. From Fig. 4, we observe that the PLE spectrum of both the samples monitored at 500 nm is very similar with a broad peak in the range 400–500 nm. The major difference in the PLE spectrum of the two samples appears when the PL intensity is monitored at 650 nm. The PLE spectrum of C_{60} doped in unpassivated PG exhibits a broad hump in the visible range 500–600 nm, while there is no such hump observed in C_{60} doped in passivated PG. These observations were in contrast with the observed absorption spectra of C_{60} doped in passivated and unpassivated PGs, as both the glasses absorb in the visible range and only C_{60}-doped unpassivated PG shows PL emission in the red region. This suggests that C_{60} in unpassivated PG is adsorbed with some structural or chemical modification such that its HOMO–LUMO transitions become allowed. In the case of C_{60} in passivated PG, there is no such modification of the C_{60} molecule. This indicates that there are no radiative centers in the C_{60} doped in passivated PG that fluoresce in the orange-red region (∼ 1.9 eV).

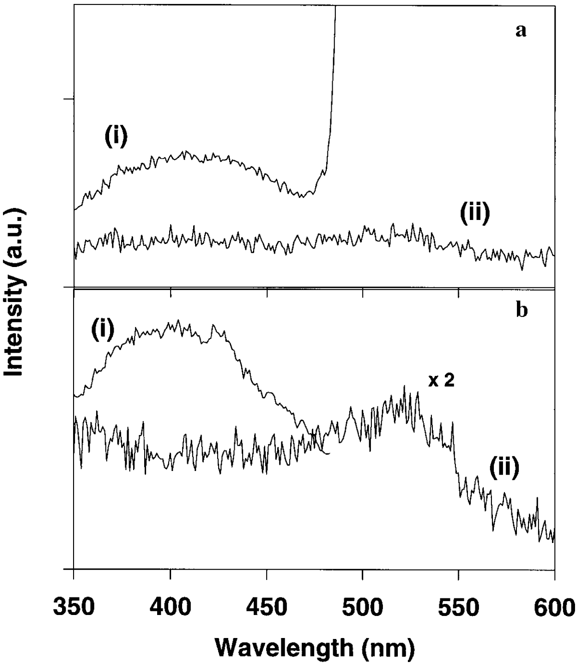

Fig. 4a,b. Photoluminescence excitation (PLE) spectra of C_{60} doped in **a** passivated and **b** unpassivated porous glass. The PL emissions were monitored at (i) 500 nm and (ii) 650 nm

From observations made from the PLE spectrum together with the PL spectrum of C_{60} doped in unpassivated and passivated PGs, we conclude that C_{60} interacts very strongly with the silica surface. By surface passivation, the interaction between C_{60} and the silica surface can be altered to study the nature of the interaction between the adsorbed molecules and the surface. The origin of enhanced and blue-shifted PL emission in these glasses seems to be due to chemical and structural modification of the C_{60} molecule. This study also rules out the model of quantum confinement of C_{60} nanocrystals formed in the pores of PG [5]. It was believed that due to quantum confinement of C_{60} nanocrystals in the pores of silica glasses the HOMO–LUMO gap of C_{60} would widen and high-energy (> 1.9 eV) radiative transitions may take place. If this model were to be true, then we would have observed similar PL and PLE spectra of C_{60} doped in unpassivated or passivated PGs because the pore diameter is the same in both types of glass.

In the light of the above model, the PL spectra of C_{60} doped and undoped surface-passivated and -unpassivated PGs, as shown in Fig. 3a–d, were quantitatively analyzed. The unpassivated and passivated pure PG and C_{60} doped in passivated PG can be fitted using two Gaussians, one centered at (peak 1) ~ 510 nm and the other at (peak 2) ~ 580 nm. As mentioned earlier the blue-green emission occurs from silanol groups. These two peaks could then be from different sites at which silanol groups are present in the form of geminal or vicinal sites [21]. The peak positions decrease in wavelength after passivation (this includes C_{60}-doped passivated PG) from 527–517 nm and 595–575 nm. After passivating the PG the FWHM widths of the peaks 1 and 2 changes from 80 nm to 70 nm and 165 nm to 145 nm respectively. This narrowing of emission widths in passivated PG as compared to in unpassivated PG is indicative of a spatially homogeneous surface of passivated PG. The spectrum of C_{60}-doped unpassivated PG (Fig. 3b) was best fitted with three Gaussians. Peak 1 shifts to 507 nm with FWHM ~ 44 nm and peak 2 shifts to 550 nm with FWHM ~ 76 nm and there is a C_{60}-related peak at 640 nm (peak 3) with FWHM ~ 172 nm. This large FWHM width for the C_{60}-molecule-related peak may due to the strongly perturbative environment seen by C_{60} molecules in unpassivated PG. It is interesting to note here that peaks 1 and 2 blue shift and narrow down after passivation and remain the same after C_{60} doping of passivated PG; however, they further blue shift after C_{60} doping of unpassivated PG. The relative ratio of intensities (with appropriate absorption correction) of peak 1 and peak 2, which are related to PG in passivated and unpassivated PG, is ~ 0.70. This decreases to 0.63 for C_{60} doped in passivated PG. In contrast, in C_{60}-doped unpassivated PG, the relative ratio of peak 1 and peak 2 decreases to 0.29. Both the blue shift and the change in relative intensities of peak 1 and peak 2 confirm that doping of C_{60} strongly modifies the host and this effect is stronger where interaction of C_{60} with the host is known to be stronger. It is found that the ratio of intensities of the C_{60}-related peak (peak 3) to the PG-related PL, peaks 1 and 2, decreases when the C_{60} concentration in PG increases. In the case of low C_{60} concentration (the data shown in Fig. 3) these ratios are 15 and 4.4 respectively. When the C_{60} concentration is increased these ratios decrease to 1.8 and 0.81 respectively. This indicates that the number of isolated C_{60} molecules in C_{60}-doped PG decreases as the concentration increases. This suggests that C_{60} molecules tend to cluster at higher concentrations. This fact is corroborated with our observation that the absorption spectrum of this sample shows features like that of a C_{60} thin film.

In conclusion, we have shown that the observed broadband PL emission from the C_{60}-doped glasses is due to the adsorption of C_{60} on a spatially inhomogeneous porous silica surface. From PL and PLE spectroscopy of C_{60} adsorbed on unpassivated and passivated PG surfaces, it is shown that C_{60} interacts strongly with the surface of unpassivated PG leading to PL emission at ~ 1.9 eV from isolated C_{60} molecules. This strong interaction can be considerably reduced by surface-passivating the PG. Our study rules out the role of quantum confinement of C_{60} nanocrystals formed in the pores of such nanoporous materials. Similarly, from the comparison of PL emissions from passivated pure PG, unpassivated pure PG and C_{60} doped in passivated PG, we conclude that the PL emission in the range > 1.9 eV has its origin in the porous glass itself.

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