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Formation and Properties of C_{70} Solidlike Species in Room-Temperature Solutions

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Recently, studies of fullerene molecules, especially C_{60} and C_{70}, have attracted great attention.[1,2] Many fascinating and sometimes unusual properties, such as formation of complexes between fullerene and solvent molecules in the solid state[3] and significant discrepancies between calculated and experimental electronic transition probabilities in both C_{60} and C_{70},[4] have been observed. It was reported[5] that C_{70} undergoes anomalous solvatochromic changes in room-temperature solvent mixtures. The characteristic phenomena were attributed to the formation of new absorbing species.[5] In this communication we report a spectroscopic study of the characteristic solvatochromic behavior of C_{70} in room-temperature mixtures of toluene and acetonitrile. It will be shown that the formation of the new absorbing species of C_{70} responsible for the anomalous solvatochromism depends not only on the concentration of C_{70} and the composition of the solvent mixtures but also on the way in which the solvent mixtures are prepared. Microstructures of the new absorbing species will be discussed.

Absorption spectra of C_{70} in mixtures of toluene and acetonitrile were recorded. While C_{70} has reasonable solubility in toluene, it is practically insoluble in acetonitrile. For C_{70} in toluene–acetonitrile mixtures, not only was significant solvatochromism observed, but also two different methods of solvent mixture preparation resulted in two distinct color changes. One method is to add acetonitrile to a toluene solution of C_{70} drop by drop, which will be referred to as the slow method. The second is the fast method, in which acetonitrile is poured into the toluene solution as rapidly as possible. For a C_{70} concentration of 7×10^{-6} M in a toluene–acetonitrile mixture with an acetonitrile composition of 70% (v/v), the slow and fast methods yielded solutions with quite different colors. The slow solution has a faint bluish color and the fast solution is a strong pinkish purple, both differing from the reddish orange color of C_{70} in neat toluene. The corresponding absorption spectra are shown in Figure 1.

The solvatochromic behavior depends strongly on the concentration of C_{70} and the composition of the mixtures. With a C_{70} concentration of 2×10^{-6} M, absorption spectra in toluene–acetonitrile mixtures with an acetonitrile composition as high as 80% (v/v) are nearly the same as the spectrum of C_{70} in neat toluene, except for slight blue shifts and minor decreases in molar absorptivities. However, significant solution color and absorption spectral changes were observed when acetonitrile composition in the mixtures was increased to 90% (v/v). For higher C_{70} concentrations, changes in solution color and absorption spectra happen at lower acetonitrile compositions. At a C_{70} concentration of 1×10^{-5} M, solvatochromic changes were observed at an acetonitrile composition of 60% (v/v). The different results of the slow and fast methods are affected little by the concentration of C_{70}. At very low C_{70} concentrations ($<1 \times 10^{-7}$ M), however, the solvatochromic behavior was not observed regardless of the acetonitrile composition.

The changes in solution color and absorption spectra are apparently due to the formation of new absorbing species. Because of the characteristic dependence of the solvatochromic behavior on the concentration of C_{70}, the new absorbing species most likely involve the participation of more than one C_{70} molecule.[7] The species formed with the slow and the fast methods should be somewhat different, corresponding to different solution colors and different absorption spectra.

The formation of the new absorbing species is reversible. After the solvatochromic changes take place at a given acetonitrile composition, decreasing the acetonitrile composition by adding toluene to the mixture changes the solution color and absorption spectrum back to those of the C_{70} monomer. However, the new absorbing species can be regenerated with the addition of more acetonitrile. The absorption spectrum of the solution containing the new species also changes upon dilution. Two different serial dilution processes were examined. One is to make serial dilutions using a blank solvent mixture with the same composition as the solution containing the new species, and the other follows a sequence of diluting C_{70} stock with toluene first before adding acetonitrile. Although the gradual absorption spectral changes resulting from the two dilution methods are somewhat different, the C_{70} monomer spectrum can eventually be obtained with both dilution methods.

The new absorbing species formed from the fast method has much higher molar absorptivities than does C_{70} monomer, corresponding to much larger transition probabilities.[6] As the acetonitrile composition increases, the new absorbing species quickly becomes the predominant, resulting in a significant increase in integrated molar absorptivities (Figure 2). Because the molar absorptivities were calculated on the basis of total C_{70} concentration, the actual molar absorptivities could be higher if the new absorbing species, as suggested above, involves more than one C_{70} molecule.

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(6) An accurate determination of the molar absorptivities for the species formed from the slow method was hindered by the formation of small solid particles that can fall out the solution in a few hours.

(7) Possible aggregates of C_{60} in room-temperature solutions have been reported.[8] However, the species discussed here are likely very different.

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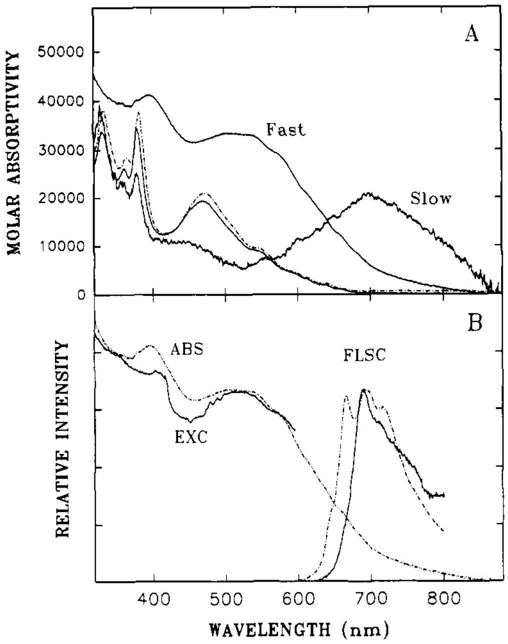

Figure 1. (A) The absorption spectra of C_{70} in neat toluene (- • -), toluene (40%)-acetonitrile (60%) (—), and toluene (20%)-acetonitrile (80%) with a C_{70} concentration of 7×10^{-6} M from the fast and slow methods. The spectrum from the slow method is on an arbitrary scale.[6] (B) The fluorescence (—), fluorescence excitation (—), and absorption (- • • -) spectra of C_{70} clusters formed from the fast method with a C_{70} concentration of 7×10^{-6} M in toluene (20%)-acetonitrile (80%). The fluorescence spectrum of C_{70} in neat toluene (- • -) is also shown for comparison.

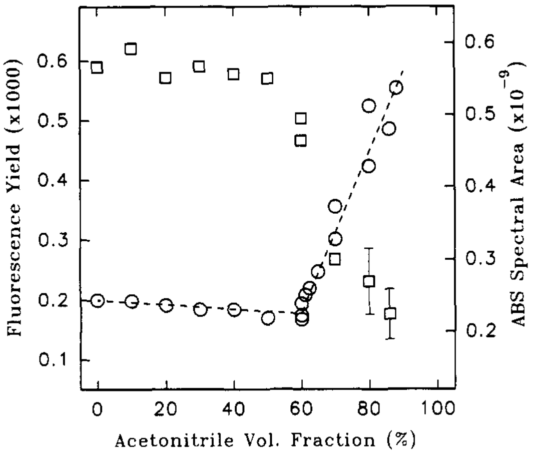

Figure 2. Fluorescence quantum yield (□) and integrated absorption spectral area (○) of C_{70} in toluene-acetonitrile mixtures as a function of acetonitrile composition.

Fluorescence and fluorescence excitation spectra, and fluorescence quantum yields were determined for the new species formed from the fast method. The emission spectra of the new species are somewhat different from those of C_{70} monomer (Figure 1). The fluorescence of the new species is also much weaker than that of C_{70} monomer. As shown in Figure 2, the observed fluorescence yield, plotted as a function of acetonitrile composition, decreases significantly upon the formation of the new species. This is opposite to the trend of increasing transition probabilities as measured by the integrated molar absorptivities. The possibility of residual C_{70} monomer in the solution being responsible for the observed fluorescence spectrum can be ruled out because not only are the fluorescence spectra of the new species and C_{70} monomer different but also the excitation and absorption spectra of the new species are in good agreement. The lower fluorescence yields of the new species are likely due to more efficient excited-state nonradiative decays. Within experimental uncertainties, the fluorescence spectra and quantum yields are essentially excitation wavelength independent. Fluorescence properties of the species from the slow method were not determined because of the wavelength region limitation of our fluorescence spectrometer.

The new species formed in both slow and fast methods are most likely microscopic aggregates of C_{70} molecules (clusters). The species formed from the slow method is probably closer to solid particles of C_{70} because precipitation was observed after storing the solution for a few hours. Less time is required for the precipitation to happen in more concentrated solutions. Precipitation can also be observed in a centrifuge field (2200 rpm for 10 min). However, the clusters formed from the fast method are much more stable with respect to gravity and small centrifuge fields. For a C_{70} concentration of 7×10^{-6} M and an acetonitrile composition of 70% (v/v), no changes in absorption spectra of the solution from the fast method were observed after it had been stored in the dark for more than 4 months. Only minor precipitation was observed in a relatively larger centrifuge field (3600 rpm for 30 min). While the solution from the slow method has higher scattering than the C_{70} monomer solution, the solution from the fast method behaves quite similar to the solution of C_{70} monomer in toluene, with only a minor increase in scattering. Although it is likely that there is a distribution of clusters formed in both the slow and the fast methods, and the distribution is probably quite sensitive to experimental parameters, the spectroscopic results are reproducible quantitatively to semiquantitatively under our experimental conditions.

The species from the fast method apparently forms an unusual suspended solution that is stable with respect to gravity and small centrifuge fields. No conversion to the species corresponding to the slow method was observed under our experimental conditions. Sonication of the solution also caused no absorption spectral changes. On the basis of the available experimental evidence we believe that the clusters formed from the fast method have a microstructure conceptually similar to that of a micelle.[9] Toluene molecules probably play the role similar to that of surfactant molecules in a micelle, mediating the repulsive interactions between C_{70} and acetonitrile molecules. Unlike in the formation of traditional micelles, toluene molecules are not responsible for the construction of the micelle-like species. Instead, the C_{70} molecules (with their large size and essentially rigid and highly symmetric structure[10]) probably play a significant role in this regard. Such a microstructure is supported by the fact that very similar solvatochromic behavior has also been observed in other mixtures such as hexane-CO_2 and benzene-acetonitrile. These mixtures are all composed of two solvents in which C_{70} is fairly soluble and practically insoluble, respectively. The species formed from the fast method must be smaller than those from the slow method, and the fast addition of acetonitrile apparently prevents the

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formation of larger aggregates as in the slow method.

The dramatic increase in molar absorptivities from C_{70} monomer to C_{70} clusters is interesting. A probable cause for such increase is a distortion of the high molecular symmetry of C_{70} monomer, the same reason for the significant increase of molar absorptivities from C_{60} to C_{70}.[11] Whether the distortion is due to interactions between neighboring C_{70} molecules or between C_{70} and toluene molecules in the inner solvation shell remains a question for further investigations.

The much smaller fluorescence yields of the clusters, despite the dramatic increase in transition probabilities, can also be explained in the context of the proposed microstructure. Two possible nonradiative decay pathways in addition to those available to C_{70} monomer are considered for the clusters. One is the dissociation of excited clusters, and the other follows a mechanism similar to that of static fluorescence quenching in excited complexes.[12] In the second pathway, localization of the excitation energy in one of the C_{70} molecules in a cluster is assumed. A photochemical study to examine the possibility of dissociation of excited clusters is in progress.

While theoretical implications of the characteristic behavior of C_{70} in the solvent mixtures remain to be explored, the clusters as solidlike species may serve as a vehicle for the understanding of C_{70} solid-state properties in a more controllable environment of a room-temperature solution. In addition, the reversible solvatochromism of C_{70} may find valuable applications in the development of optical switching technology.

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