C_{70} in solvent mixtures

SIR — The fullerene $(5,6)$-C_{70} exhibits unusual solvatochromism in acetonitrile–toluene mixtures at room temperature. At a C_{70} concentration of 6.6×10^{-6} M, an increase of acetonitrile volume fraction (x_{ace}) in the mixtures up to 60% causes essentially no spectroscopic change of the

Absorption spectra of C_{70}: A, in room-temperature acetonitrile–toluene mixtures as a function of acetonitrile volume fraction (x_{ace}); and B, in acetonitrile (70%)–toluene (30%) mixture as a function of C_{70} concentration. C_{70} is from Aldrich with an estimated purity >98%. Acetonitrile and toluene, both from B&J (spectrophotochemistry grade), are used as received because no interference from possible impurities in the wavelength region of interest is found on the basis of absorption and emission spectroscopic measurements of the solvents. Absorption spectra are obtained on a computer-controlled Shimadzu UV2101-PC UV-Vis spectrophotometer.

solution. The absorption spectrum at x_{ace} = 60% is almost the same as the spectrum in neat toluene, except for a very minor blueshift (part A in the figure). But, as x_{ace} increases from 60 to 70%, the C_{70} solution undergoes a dramatic colour change, from reddish orange to pinkish purple, and the corresponding absorption spectra show completely different features. The spectrum of the purple solution (x_{ace} = 70%) is much broader, with substantial absorption in the 550–800-nm region and with-

out the structures in the 300–400-nm region. In addition, the spectral shape change is reversible, and accompanied by a significant increase in molar absorptivity, corresponding to much enhanced transition probabilities. The purple solution is macroscopically homogeneous and transparent, and is thermodynamically stable, with no changes in time or through sonication.

The observed colour and spectral changes are obviously not a typical result of solvatochromism. The phenomenon can be attributed to the formation of a new absorbing species at $60\% \leqslant x_{ace} \leqslant 70\%$. A further increase of x_{ace} from 70 to 97% does not fundamentally change the absorption spectrum any further (part A in the figure), but apparently enhances the absorption of the new species. From a C_{70} concentration dependence study, we find that the formation of the new species depends strongly on the solution concentration (part B in the figure). The lower the concentration, the smaller is the contribution of the new species. For a very dilute C_{70} solution ($\leqslant 8 \times 10^{-8}$ M), the absorption spectrum at x_{ace} = 70% is close to the spectrum in neat toluene. The results indicate that the formation of the new species involves more than one C_{70} molecule.

We are reluctant to assign the new species to C_{70} dimers. Rather, it is more likely that the purple solution is a result of absorption by a distribution of solvated C_{70} clusters. We use the term 'cluster' (which refers to an aggregate of a few C_{70} molecules) because the corresponding solution is quite different from a conventional colloidal solution. The purple solution formed at x_{ace} = 70% is macroscopically indistinguishable from a dilute solution of C_{70} in neat toluene, except for the difference in colour (the C_{70} toluene solution is reddish orange).

The formation of C_{70} clusters in a solvent mixture can probably be represented by a microscopic picture similar to the one for micelles. Because of rather poor solubility of C_{70} in acetonitrile, the C_{70} clusters are probably surrounded by shells of toluene molecules, which maintain the stability of the clusters in a

homogeneous solution. Although the formation of clusters in such a low concentration room-temperature solution is clearly a result of vastly different solubilities of C_{70} in acetonitrile and toluene, it is a rather unusual phenomenon that has not been observed in other systems, and is probably dictated by the shape, dimension and other intrinsic properties of C_{70} molecules[1,2]. Absorption of C_{70} clusters is also observed in other solvent mixtures composed of two components in which C_{70} has very different solubilities, such as room-temperature mixtures of hexane and liquid carbon dioxide at about 150 bar.

The properties of the C_{70} clusters should be close to those of solid-state C_{70}. Our observation thus offers an attractive alternative for the investigation and application of C_{70} solid-state properties[3–5]. In addition, the characteristic and reversible solvatochromism of C_{70} may be valuable in optical-switching applications.

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Split second?

SIR — In modern Olympic athletic events it is now customary to time competitors to an accuracy of 0.01 second — a few hundredths of a second can be crucial in deciding which athlete comes first. It seems to have gone unnoticed, however, that the usual starting procedure, which depends on a starting pistol, introduces differential delays owing to the finite speed of sound.
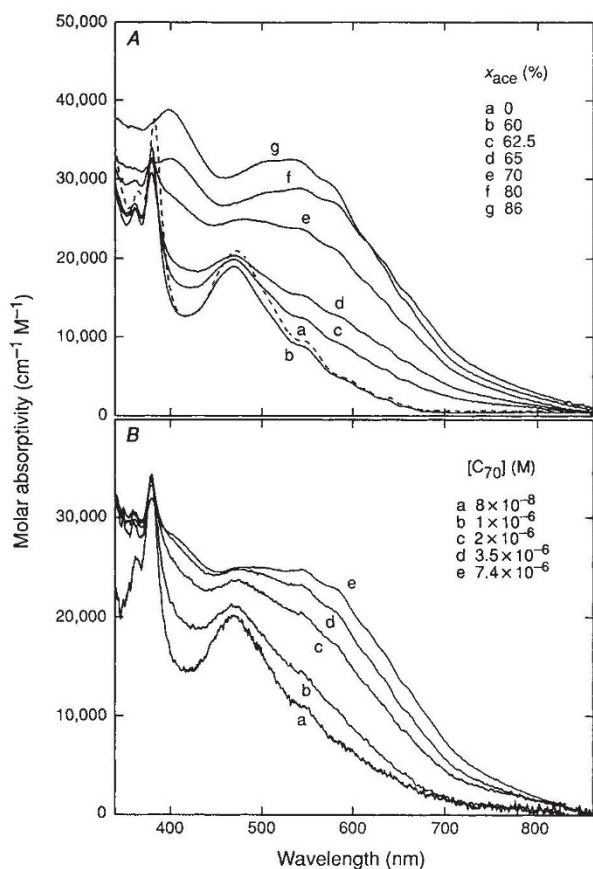
The starter usually stands just behind the line of athletes, close to the innermost lane (lane one). The loudspeakers placed in the blocks are primarily used to tell the athletes to go to their starting positions. The athletes run on hearing the shot. The typical width of a lane is 1 metre and the velocity of sound 340 metres per second, so an athlete in lane eight will hear the shot 0.02 seconds later than an athlete in lane one. Can we, then, be sure that we have correctly identified the winner in the event of a close finish?

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