

Aggregation Properties of an Amphiphilic Methanofullerene Derivative in THF–H₂O Solvent Mixtures

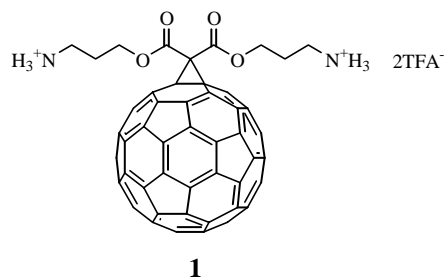
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Abstract: Amphiphilic methanofullerene **1** exhibits strong tendency to form aggregates in THF–H₂O solvent mixtures. Two different aggregation processes induced by either varying the solvent composition or upon standing have been found. Concentration has great influence on the aggregation process. Paralleling to the UV-Vis changes, an unusual solvatochromism has been observed in these two different processes.

Keywords: Aggregate, solvatochromism, amphiphilic methanofullerene.

Water-soluble fullerenes not only have a number of important applications in biological chemistry¹, but also form ordered aggregate structures that can be utilized in materials science². There are reports that some water-soluble fullerene derivatives can form ordered structures in water, such as vesicle, nanorod and nanoparticle²⁻⁵. However, relatively few reports on the aggregation process have been reported. Knowledge of factors that affect the cluster formation in solution is of considerable importance in evaluating the biological applications of these water-soluble compounds. Recently, water-soluble methanofullerene derivative **1** has been found as an excellent inhibitor of nitric oxide synthase¹. In the present work, we report the aggregation behaviour of methanofullerene **1** in THF–H₂O solvent mixtures monitored by UV-Vis spectroscopy.



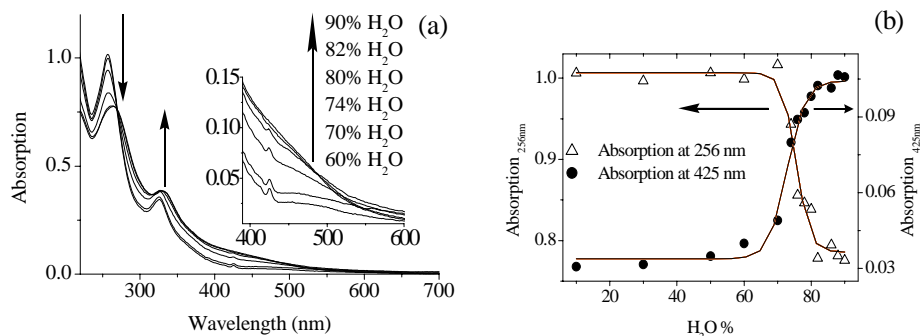
Methanofullerene **1** was synthesized according to the described procedures⁶. A series of solutions of **1** in binary mixtures of THF–H₂O were prepared by diluting 1 ×

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10^{-4} mol/L THF mother solution with THF–H₂O solvent mixtures at appropriate volume ratios.

The sharp UV-Vis absorptions of methanofullerene **1** in THF are located at 256, 324 and 425 nm. This result is in agreement with the reported spectroscopic characteristics of methanofullerene derivatives present in solution in the form of monomer⁷. But some absorption maxima mentioned above in the UV-Vis spectrum of **1** broadened and even disappeared in water-rich binary mixtures of THF–H₂O. The UV-Vis spectra of a series of THF–H₂O solutions of 1×10^{-5} mol/L **1** were measured and some representative UV-Vis spectra are presented in **Figure 1a**. Plots of UV-Vis absorptions at 256 nm and 425 nm *versus* solvent composition in binary THF–H₂O mixtures are shown in **Figure 1b**.

Figure 1 (a) UV-Vis absorption spectra of 1×10^{-5} mol/L **1** in THF–H₂O solvent mixtures; (b) plots of UV-Vis absorptions at 256 nm and 425 nm *vs.* solvent composition in THF–H₂O solvent mixtures



By gradually increasing the water content of THF–H₂O solutions of **1** while the concentration was kept at 1×10^{-5} mol/L, the UV-Vis absorptions of **1** started to change. The UV-Vis spectra of **1** are nearly overlapped when water content ranges from 10% to 60%, and almost remains the same when water content is above 82%, but they change dramatically when the water content is between 60% and 82%. Within the latter range, upon increasing the water content, the intensity of absorptions at 324 nm and 425 nm increased with a concomitant absorption decrease at 256 nm. Correspondingly, the peaks at 256 nm and at 324 nm shifted to 265 nm and 331 nm, respectively.

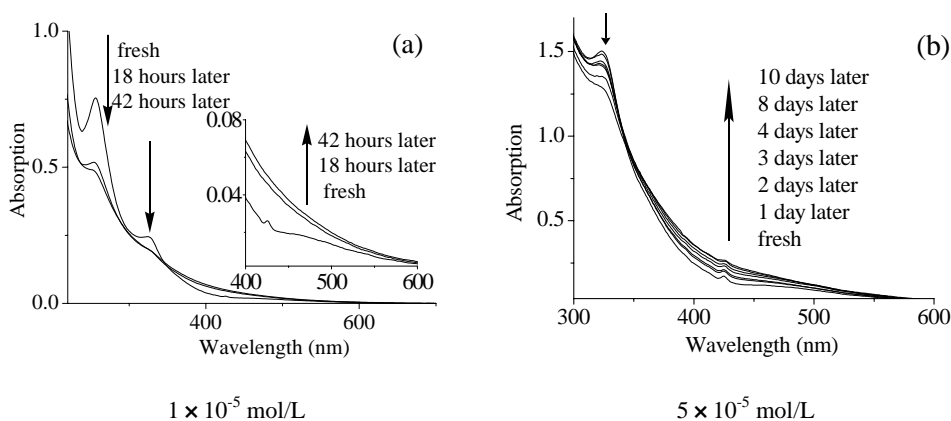
The broadened UV-Vis absorptions, decreased the intensity of absorptions in ultraviolet region and increased absorptions in visible region of **1** in H₂O rich solutions (**Figure 1a**) indicated that aggregates were formed in these solutions⁸⁻¹⁰. The two turning points for both curves in **Figure 1b** indicated that the aggregation formation of compound **1** is a nonlinear process. The forming of the aggregation begins only at about 60% H₂O–40% THF (v/v) and is essentially completed at about 82% H₂O–18% THF (v/v).

Interestingly, paralleling to the UV-Vis absorption changes of the corresponding solutions, solvatochromism could be visually observed. Upon increasing the water content, the solution color of compound **1** in THF–H₂O solvent mixtures changed

dramatically from colorless (< 60% H₂O) to yellow. This unusual solvatochromism may result from the formation of aggregates in solutions due to the auto-association of C₆₀ skeletons.

The UV-Vis spectra of compound **1** in the water-rich (H₂O% > 82 %) solutions of THF-H₂O mixtures remain clear and macroscopically homogeneous for more than one month with no precipitation. However, when the water content is below 60%, monomeric **1** can self-assemble to aggregates upon standing. Furthermore, the aggregation process depends on the concentration of the solution in storage. **Figure 2** shows the UV-Vis spectral changes of methanofullerene **1** upon standing in 50% THF-50% H₂O (v/v) at different concentrations.

Figure 2 Changes of UV absorption spectra of **1** at different concentrations in 50% THF-H₂O at 20±1 °C



The UV-Vis absorptions of **1** decreased at 256 nm and 324 nm while increased at 426 nm upon standing. This spectral change trend is different from that by varying the solvent composition of the binary THF-H₂O mixtures. For the 1×10^{-5} mol/L **1** in 50% THF-50% H₂O (v/v), the aggregation process was completed less than one day. In contrast, for the 5×10^{-5} mol/L **1** in 50% THF-50% H₂O (v/v), the aggregation process was much slower. The UV-Vis spectra exhibited only little decrease at 324 nm and little increase at 425 nm along with observable peak at 425 nm even after 10 days of storage. It is obvious that the transformation from monomer to aggregates for **1** is faster at lower concentration. With increasing storage time, a similar color change could also be observed.

It is important to note here that the two aggregation processes described above are entirely irreversible. Once the cluster had been formed, it was, however, impossible to disintegrate it again by diluting with THF or H₂O. This phenomenon is different from the aggregation behavior of C₆₀¹¹. The formed aggregate could not be disassembled by stirring or sonication.

Solutions of compound **1** in THF-H₂O solvent mixtures demonstrate rather unusual UV-Vis spectra changes when compared with those in other binary mixtures. Although

aggregation process of **1** was observed when the water content was increased in solvent mixtures of DMF–H₂O, DMSO–H₂O and CH₃OH–H₂O, the UV-Vis spectrum of **1** did not change essentially upon standing in these binary mixtures. The unusual aggregation process of compound **1** in THF–H₂O mixtures, which depends on storage time and concentration, indicates that THF is a quite special solvent from other organic solvents in the aggregation process.

To the best of our knowledge, the aggregate formation of an amphiphilic fullerene derivative in solution induced upon standing and critically depended on the concentration has not been reported before.

In summary, the aggregate formation of the amphiphilic C₆₀ derivative **1** in THF–H₂O solvent mixtures induced by either varying the solvent composition or upon standing has been found and can be monitored by UV-Vis spectroscopy. The aggregation process from monomeric **1** to clusters heavily depends on its concentration in THF–H₂O solvent mixtures. Paralleling to the UV-Vis changes, unusual solvatochromism in these binary solvent mixtures also has been observed.

Acknowledgments

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