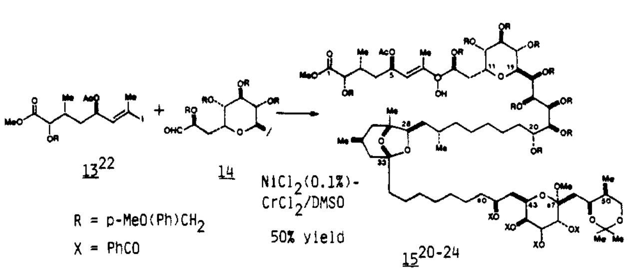

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(20) Cheon, S. H.; Christ, W. J.; Fujioka, H.; Hawkins, L. D.; Jin, H.; Kishi, Y.; Leder, J.; Taniguchi, M.; Ueda, K., Uenishi, J., unpublished results. The coupling of **14** with the β-iodo enone corresponding to **13** in DMF-(Me)$_2$S was equally satisfactory to give about a 5:1 mixture of 8α- and 8β-allylic alcohols in about 50% yield.

(21) All the new compounds in this paper gave satisfactory spectroscopic data.

(22) The synthesis of this substance will be published elsewhere: Christ, W. J.; Hawkins, L. D.; Jin, H.; Kishi, Y.; Taniguchi, M., manuscript in preparation.

(23) The stereochemistry of the alcohol was established by chemical correlation with a known compound.

(24) For the numbering used in the paper, see the structure **15**.

Micelle-Mediated Resonance Raman Spectroscopy: A New Approach for Characterizing Low Levels of Luminescent Compounds

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It is well-known that the vibrational spectra produced by Raman scattering spectrometry provide abundant information on the structure of molecules and can be used to characterize them. The inherent weakness of the Raman signal is the major shortcoming of this potentially powerful technique. Two methods used to enhance Raman signals include surface enhanced Raman scattering (SERS)[1-6] and resonance Raman scattering (RRS).[7-17]

Table I. Fluorescence Quenching in Aqueous Micellar Media

concn, ppm	rel luminescence intensity[c]
[ZnTPPS$_4$][a]	
<1	<0.001
5	<0.001
10	5.5
50	16.2
[acenaphthylene][b]	
<1	<0.001
25	<0.001
50	<0.001
200	<0.001

[a] The zinc tetraphenylporphyrin tetrasulfonic acid (ZnTTPS$_4$) was dissolved in 5% aqueous brominated Brij 96 containing 2 × 10^{-3} M 5-DOXYL stearic acid and 4 × 10^{-3} M 4-phosphonooxy-TEMPO monohydrate. [b] Micellar solution consisted of 0.2 M thallium dodecyl sulfate and 0.7 M sodium dodecyl sulfate. [c] Measured with a Perkin-Elmer LS-5 spectrofluorimeter (λ_{ex} = 420 nm, λ_{em} = 608 nm, slits = 10 nm, setting = 1.0 full scale). One part per million ZnTPPS$_4$ in H$_2$O gives a fluorescence intensity of 90, while one part per million acenaphthylene in methanol gives a fluorescence intensity of 6.

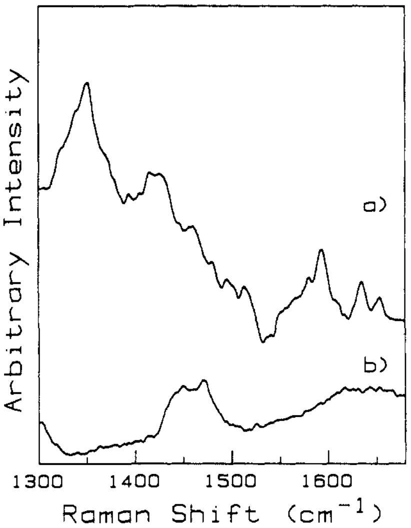

Figure 1. (a) Resonance Raman spectrum of 4.3 × 10^{-5} M ZnTPPS$_4$ in brominated Brij micellar cocktail. (b) Raman spectrum of micellar solution blank. Both spectra were obtained with 402-nm excitation (4-mW average power) and a spectral band-pass of ~10 cm^{-1}. Spectra are the sum of two scans. The composition of the micellar cocktail is given in Table I.

While both methods can enhance Raman signals up to 6 orders of magnitude, there are a number of experimental and theoretical limitations associated with each. For example, the fluorescent background produced when exciting on the electronic absorption band of a compound generally negates enhancement advantages of resonance Raman scattering. Consequently, a significant amount of research has been done to develop techniques which partially eliminate or circumvent the problem of luminescence.[18-27]

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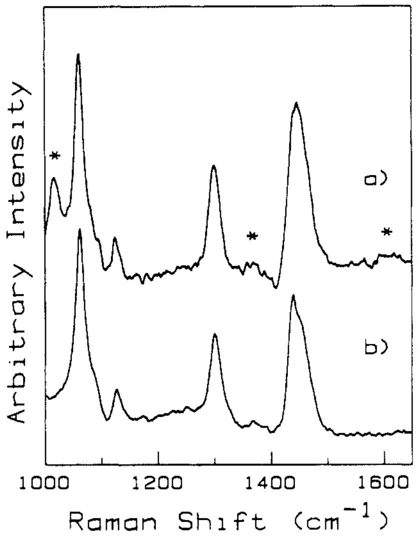

Figure 2. (a) Resonance Raman spectrum of 6 × 10^{-4} M acenaphthylene in a thallium–sodium dodecylsulfate co-micelle. (b) Raman spectrum of micellar solution blank. Conditions are the same as in Figure 1. Bands attributable to acenaphthylene are denoted by *.

In this work, we report a new approach to resonance Raman spectroscopy which makes use of specially functionalized micelles.[28] It is thought that this micellar method will make RRS a relatively sensitive and widely applicable technique in which an analyte's luminescent properties are no longer of critical importance. There are several ways functionalized micelles can be used to advantage in RRS. First, micelles can shift both absorption and luminescent band maxima.[29,30] Shifting the absorption band closer to the laser excitation line gives one a greater resonance effect. For example, the Soret band of methanolic zinc tetraphenylporphyrin tetrasulfonic acid (used in this study) undergoes a bathochromic shift of 6 nm when in aqueous micellar solution. Even this modest shift resulted in a 2-fold change in the extinction coefficient at a fixed wavelength. Spectral shifts an order of magnitude higher have been reported. Shifting the background luminescence away from the Raman bands is equally advantageous. Micelles can also alter an associated compound's luminescent lifetime and quantum yield.[29,30] In RRS it is desirable to significantly decrease both of these. This is accomplished by utilizing surfactants containing heavy atoms and/or free radicals. This quenching effect is shown in Table I. Micelles also can enhance nonradiative processes by bringing a luminescent compound into close contact with other added quencher molecules. Mechanistically, this process is somewhat akin to that of micellar inhibition and catalysis.[31] Micelles allow solubilization of hydrophobic solutes in water (a good Raman solvent) as opposed to organic solvents which produce strong, interfering Raman bands. Indeed, the signal to noise ratio can be increased up to 2 orders of magnitude in aqueous micellar solution. This was first demonstrated by Beck and Brus for transient spontaneous Raman scattering.[32] Micelles also can stabilize transient species that are difficult to observe in other solvents (e.g., radical ions), as well as preventing photodecomposition and altering the fluorescence depolarization and pH profile of a variety of compounds.[29,30]

Judicious use of one or more of the aforementioned micellar effects allows one to record resonance Raman spectra that were previously difficult or impossible to obtain. Figure 1 shows the first reported resonance Raman spectrum (to our knowledge) of a 4.3 × 10^{-5} M solution of zinc tetraphenylporphyrin tetrasulfonic acid ($ZnTTPS_4$) obtained with direct Soret excitation.[33] No evidence of photodecomposition (a common problem with tetraphenylporphyrins upon laser irradiation) was observed in the absorption spectra of samples prepared in Brij "cocktail" (see Table I for the exact composition of the micellar solutions). The prominent ν_4 band at 1360 cm^{-1} and ν_2 and ν_{11} bands at ~1586 nm, as well as a number of weaker bands, are easily observable. The background from the micellized surfactant is minimal (Figure 1). Figure 2 shows the resonance Raman spectrum of 6 × 10^{-4} M acenaphthylene in another micellar cocktail.[33] Characteristic bands are noted at 1020 cm^{-1} and above 1580 cm^{-1}. Although the surfactant bands are more prominent in this spectrum, note that the surfactant is several orders of magnitude more concentrated than the acenaphthylene.

The use of functionalized micelles in RRS is simple and highly advantageous. A knowledge of the physical and chemical properties of micelles[34] is beneficial in that it allows one to choose the optimum combination of effects to enhance RRS. It is hoped that this will make RRS an even more widely applicable technique for the study of molecular structure. It may also allow the first effective use of Raman in hyphenated techniques such as LC-resonance Raman.

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[28] Functionalized micelles contain surfactants with specific functional groups. The purpose of the functional group is to enhance the desired micellar effect. For example, a surfactant containing a heavy atom will tend to enhance fluorescence quenching of certain compounds.

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[33] A Molectron UV-24 nitrogen laser is used to pump a Molectron DL-II dye laser. A backscattering geometry is used to illuminate the sample. The scattered radiation is collected and passed through a polarization scrambler before being focused into a SPEX 1403 scanning monochromator. a photomultiplier (Hamamatsu R-928) in a cooled housing is used for signal detection. The output of the PMT is directed into a EG&G Model 162 boxcar with a Model 164 plug-in integrator card. The boxcar is triggered by a photodiode which is triggered by the laser pulse. The output of the boxcar is fed into a SPEX Datamate (DM-1), which controls the monochromator and stores the collected data. The data is then transferred via an RS-232 interface to an Apple II series computer for storage on a floppy disk and subsequent graphic manipulation. Excitation was at 402 nm, and the solvent was as indicated in the footnote of Table I.

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Ethylene Biosynthesis. 7. Secondary Isotope Effects

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In a continuing investigation of the mechanism of the biosynthesis of ethylene, the plant ripening hormone, from 1-aminocyclopropanecarboxylic acid, the study of isotope effects was undertaken in order to provide insight into the rates of various bond-breaking steps. While the applicability of the concept of "rate-limiting step" to enzymatic reactions has been questioned[2] and redefined[3] (and there is little doubt an ethylene-forming enzyme exists[4]), such studies were expected to elucidate some mechanistic detail as well as measure the validity of a model for ethylene biosynthesis.[6]

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