

Figure 1. Equivalents of acetone formed (with respect to moles of $\text{H}_2\text{-PtCl}_6$ used) vs. time for three intensities of 488-nm light. (0.046 (●), 0.138 (▲), and 0.276 W (■)) from an Ar^+ laser. All trials contain 7 mM H_2PtCl_6 and 7 mM CuCl_2 in 5 mL of neat isopropyl alcohol, with a slow stream of O_2 passing over the reaction mixture. The solutions were maintained at room temperature. Catalyst stability is indicated by the linearity of these curves ($\Phi^P = 0.05$).

temperature, there does not exist a thermal pathway to acetone formation in the presence of $\text{H}_2\text{PtCl}_6/\text{CuCl}_2/\text{O}_2$. The reaction can be easily driven, however, by visible light. The reaction is found to proceed with wavelengths of light as low as 514 nm when a monochromatic source is employed. This corresponds to the lowest energy absorption band in the $[\text{PtCl}_6]^{2-}$ complex. The absorption in this region has previously been assigned to a triplet ligand field transition ($^1A_{1g} \rightarrow ^3T_{2g}$);⁵ although there are strong indications in the $[\text{PtCl}_6]^{2-}$ photochemistry literature that there exists a component of ligand \rightarrow metal charge-transfer character in this region of the spectrum.⁶ Product quantum yields as high as 0.1 have been observed for this reaction (at 488 nm), with values of ~ 0.05 (Figure 1 and Table I) being more standard. Turnover numbers in excess of 150 have been observed when white light³ is employed with only a slight decrease in catalytic activity at the end of the reaction period. Catalyst stability is further indicated by the data in Figure 1 which shows a linear relationship between turnover number and reaction time over a 60-h period. Note that the slopes of the lines in Figure 1 change linearly with light intensity demonstrating a constant value of the product quantum yield over the intensity regime employed and a turnover rate that is directly proportional to the light intensity. The linearity of these data with respect to both time and light intensity further substantiates the high product specificity noted earlier.

The reaction is found to be fairly sensitive to the amount of CuCl_2 present. If either the CuCl_2 or O_2 is omitted from the reaction, then Pt-metal is observed to form along with a stoichiometric amount of organic products. As the CuCl_2 concentration is increased the turnover rate is observed to increase linearly. This phenomenon appears to saturate at an $\sim 2:1$ ratio of CuCl_2 to $[\text{PtCl}_6]^{2-}$. Addition of an excessive amount of CuCl_2 causes the solution to turn brown with a concomitant loss of catalytic activity. ^{195}Pt NMR studies demonstrate that Cu^{2+} cannot oxidize $[\text{PtCl}_4]^{2-}$. This result, taken along with a consideration of standard redox potentials which indicates that CuCl_2 cannot thermodynamically oxidize $[\text{PtCl}_4]^{2-}$, can be best explained by assuming that Cu^{2+} is oxidizing a Pt(III) chloride complex to regenerate $[\text{PtCl}_6]^{2-}$. The presence of a Pt(III) intermediate is consistent with previous photoaquation results^{6,7} and suggests that alcohol oxidation may be occurring via a free radical mechanism. Support for this mechanism is provided by the observation that extensive irradiation of the isopropyl alcohol system yields trace amounts of acetaldehyde suggesting methyl free radical loss from the free radical alcohol. The exact details of the total catalytic cycle are currently under investigation.

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Chiral Pyrene Excimer in the γ -Cyclodextrin Cavity

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Several multicomponent complexes of cyclodextrins have recently been reported.²⁻¹⁵ The formation of the 2:1 and/or 2:2 complexes of pyrene with γ -cyclodextrin (γ -CDx) have been proved by the pyrene excimer fluorescence.¹⁶⁻¹⁸ In this paper, we report the formation of a chiral pyrene excimer in the cavity of γ -CDx, which shows extremely intense circular polarization in fluorescence.

A dilute aqueous solution of pyrene showed only monomer fluorescence whose lifetime was 127 ns under aerobic conditions. Upon addition of γ -CDx, a broad excimer fluorescence band centered at 474 nm appeared at the expense of the monomer fluorescence. The fluorescence maximum of the pyrene excimer in the γ -CDx solution shifted to longer wavelength compared with those in organic solvents (462-467 nm). A fluorescence decay curve of the excimer in the aqueous γ -CDx solution consisted of two rise and one decay components: $\tau_1 =$ very fast ($f_1 =$ ca. -0.7), $\tau_2 = 24$ ns ($f_2 =$ ca. -0.3), and $\tau_3 = 112$ ns ($f_3 = 1.00$). The fast rise component may be due to the pyrene dimer in the CDx cavity which yields an excimerlike state immediately after exciting. Interestingly, parts of the pyrene molecules form the excimer state through a relatively slow dynamic process, a rise time being 24 ns.

An extremely intense circularly polarized fluorescence (CPF) signal was measured at the excimer region in the γ -CDx solution (Figure 1).¹⁹ The ordinate in Figure 1 is Kuhn's dissymmetry factor, $g_{em} = 2(I_L - I_R)/(I_L + I_R)$.²⁰ No or very weak CPF signal was measured at the monomer region, which is in good agreement with the results for (+)- and (-)-1-(1-hydroxyhexyl)pyrenes in methanol²¹ and *N*-acetyl-D- and *N*-acetyl-L-pyrenylalanines in

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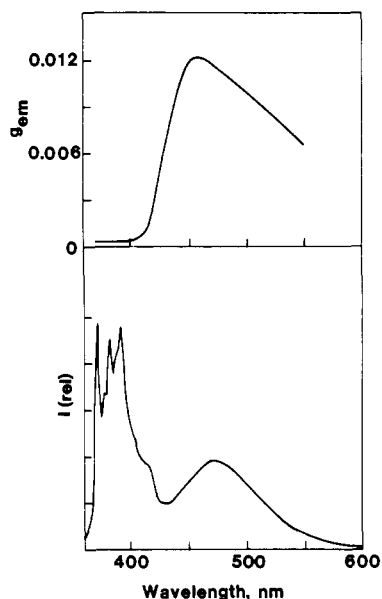


Figure 1. Fluorescence (bottom) and CPF (top) spectra of pyrene (2×10^{-6} M) in aqueous γ -CDx (1×10^{-2} M) solution at 25 °C.

toluene and dimethylformamide.²² This also suggests that the large g_{em} in the present system is neither due to an artifact caused by a linear polarization nor due to an electronic perturbation by the γ -CDx cavity on an achiral excimer. The electronically induced CPF has been reported for the systems of an achiral fluorophore (fluorescein) in a chiral solvent (phenethylamine)²³ and a 1:1 inclusion complex of fluorescein and β -CDx.²⁴ The $|g_{em}|$ values for the electronically induced CPF, however, are significantly smaller (10^{-4} – 10^{-3}) than that for the present system (0.0071–0.012). Consequently, it can be concluded that the pyrene molecules in the γ -CDx cavity form the excimer having an asymmetrically twisted configuration.

The intramolecular excimer systems can be regarded as the model guests for studying the 2:1 = guest:CDx complexes.^{25–27} We used 1,3-bis(1-pyrenyl)propane (P(3)P). Since P(3)P is completely insoluble in water, a dilute aqueous dispersion (10^{-6} M) shows only excimerlike fluorescence centered at 478 nm due to the P(3)P aggregates, which shows a multiexponential fluorescence decay.²⁸ In the presence of γ -CDx (10^{-2} M), however, the fluorescence from the locally excited state of P(3)P was observed along with the intramolecular excimer fluorescence with a maximum intensity at 490 nm. The fluorescence decay of the P(3)P excimer was single exponential ($\tau_f = 159$ ns) in the presence of γ -CDx and no rise of the excimer was observed, suggesting that the intramolecular dimer state is formed in the γ -CDx cavity in the ground state. A relatively weak CPF signal was observed for the P(3)-P- γ -CDx system, g_{em} being ca. +0.003 at the excimer region.

Recently, an induced circular dichroism (ICD) of the pyrene dimer formed in the γ -CDx cavity has been reported.¹⁸ A very small absorption dissymmetry factor of ICD (ca. 6×10^{-5} at the 1L_a band)²⁹ indicates a weak asymmetric nature of the pyrene dimer in the γ -CDx cavity in the ground state. Upon excitation of a pyrene molecule, the reorientation of two pyrene molecules may occur in the γ -CDx cavity to form thermodynamically

metastable excimer state. In fluid media, the pyrene excimer takes a sandwichlike configuration. In the γ -CDx cavity, however, the sterically restricted environment may not allow formation of a symmetric sandwich excimer. An asymmetrically twisted configuration seems to be taken under the conditions. In the case of P(3)P, an alkyl chain, which links two pyrenyl groups, seems to prohibit the configurational change of P(3)P included in the γ -CDx cavity. This may cause the smaller g_{em} value and the absence of the rise of the intramolecular excimer fluorescence. No wavelength dependence of the g_{em} value over the whole excimer region was observed for the P(3)P- γ -CDx system, suggesting only one fluorescent state which shows CPF. As Figure 1 shows, however, the g_{em} value for the pyrene- γ -CDx system decreases at longer wavelength. There may be two fluorescent states, one is the excimer state and another is the dimer excited state, whose configuration is almost the same as that of the ground-state dimer of pyrene in the γ -CDx cavity. The rise of the pyrene excimer fluorescence observed in the decay curve may be ascribed to the dynamic formation of the excimer state in the γ -CDx cavity which seems to be a considerably tight environment for two pyrene molecules.

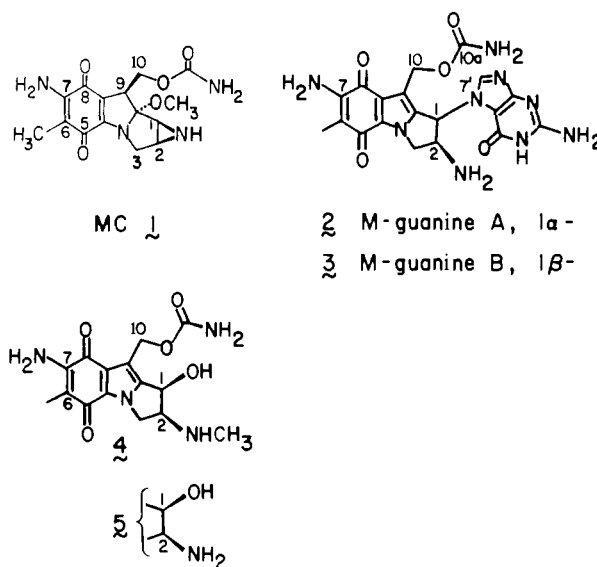
Use of Differential Second-Derivative UV and FTIR Spectroscopy in Structural Studies of Multichromophoric Compounds

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Mathematical second derivatization of absorption spectra has primarily been used as a tool for enhancing resolution or clarifying maxima in strongly scattering samples. However, the technique can be exploited to a much greater extent, especially when coupled with subtractive methods. This is shown by the usage of differential second-derivative UV (differential SEDUV) and FTIR (differential SEDIR) spectroscopy in the microgram-scale structure determination of complex molecules exemplified by the mitomycin C (MC, 1)/guanine adducts 2 and 3. The method



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described can be performed on most computerized UV and IR spectrometers without weighing of samples and should be generally applicable to a wide variety of problems.

Treatment of MC with the dinucleoside phosphate d(GpC) under acidic conditions yields a complex mixture from which were isolated two major adducts M-guanines A 2 and B 3¹ (M denotes