that other intermediates which do not include $Cl^-$ or $Br^-$ as an axial ligand are generated under the catalytic conditions.[15]

Recently, some efficient alkane oxidation systems have been developed using manganese porphyrins.[16] The systems with transition metal-substituted polyoxometalate catalysts[17] and the Gif systems[18] are also efficient. However, our system seems to be the most efficient metal-catalyzed alkane oxidation system in terms of turnover numbers and yields based on substrates. Moreover, this system offers various practical advantages for use as a synthetic reagent, such as mild conditions, simple handling procedures, and the use of a highly stable and tractable oxidant. Studies to extend the scope of this system and to elucidate the mechanistic details are in progress in our laboratory.

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## A New Method for Controlling the Orientation of Functional Molecules in Langmuir-Blodgett Films

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The Langmuir-Blodgett (LB) method has been widely studied as one of the most versatile techniques to fabricate organic thin films with well-controlled compositions, structures, and thicknesses.[1,2] Due to these features the LB technique has been used to construct prototypes of molecular electronic and bioelectronic devices.[3-12]

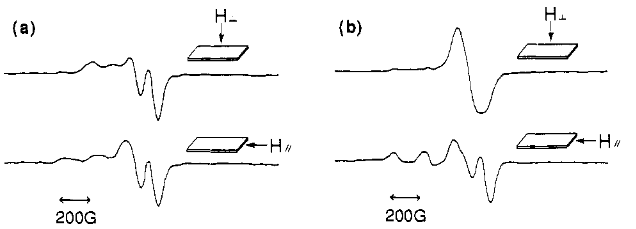

**Figure 1**. First-derivative ESR spectra of the LB film (40 layers on both sides) at the angles of 0° and 90° between the external magnetic field and the film surface: (a) PM/cadmium icosanoate = 1.5/10; (b) PM/cadmium icosanoate/hexatriacontane = 1.5/10/2.

Typical LB films consist of amphiphilic molecules with long alkyl chains. The alternative is to employ lightly-substituted molecules or molecules without long alkyl chains, which enables dense packing of functional molecules in the films.[13-17] Further, this strategy makes the orientation of the chromophores different from that obtained for the usual LB films of amphiphilic molecules. Such nonamphiphilic molecules have been mixed with film-forming molecules such as fatty acids to obtain good LB films.[18-20]

A great deal of effort has been made to control the orientation of functional molecules in LB films. Chemical modification seems to be very efficient in this respect. The orientation of anthraquinone has been controlled by changing the position of the attached alkyl chains.[21] Physical methods have also been employed for this purpose.[22-24]

In this communication we report that a small amount of long-chain *n*-alkane, when added in the preparation of monolayers, can drastically change the orientation of a dye molecule in the LB films.

[Tetrakis(3,5-di-*tert*-butylphenyl)porphinato]copper(II), PM,[25] was used as a dye molecule. A chloroform solution of molar ratio PM/icosanoic acid/*n*-alkane = $1.5/10/r$ ($0 \leq r \leq 5$) was spread onto an aqueous subphase of pH 6.0 containing $4.0 \times 10^{-4}$ M of $CdCl_2$ and $5.0 \times 10^{-5}$ M of $KHCO_3$ at 17 °C. The monolayers

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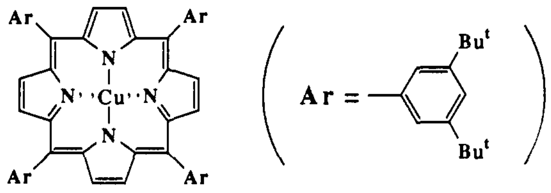
were transferred by vertical dipping at a surface pressure of 25 mN/m on a polyethylene terephthalate sheet precoated with five layers of cadmium icosanoate.[26]



**PM**

We have employed ESR spectroscopy to determine the orientation of PM molecule in the mixed LB films. The hyperfine interaction of the unpaired 3d electron of copper(II) ion with its own nucleus causes the signal to split into four lines.[27] This hyperfine coupling as well as the $g$ value are highly anisotropic for the planar copper(II) complexes: the hyperfine coupling constant is a factor of 10 smaller when the external magnetic field is perpendicular to the normal of the macrocycle plane ($A_\perp^{\mathrm{Cu}} \approx 2 \times 10^{-3}$ cm$^{-1}$) compared with the parallel case ($A_\parallel^{\mathrm{Cu}} \approx 2 \times 10^{-2}$ cm$^{-1}$). These features have been used to investigate the orientation of planar copper complexes in LB films.[28-31] The X-band ESR spectra were obtained with a Varian E-4 ESR spectrometer at room temperature.

A tilt of the macrocycle plane of PM with respect to the surface normal of the mixed LB film without $n$-alkane is consistent with the spectral data shown in Figure 1a. The hyperfine splitting due to copper is clearly observed in both of the spectra with the external magnetic field perpendicular ($H_\perp$) and parallel ($H_\parallel$) to the film surface. The $H_\perp$ spectrum shows a signal located at slightly higher field with a smaller coupling constant compared with the $H_\parallel$ spectrum. The angle between the normal of the macrocycle plane and that of the film surface is estimated to be around 50° by a preliminary simulation considering the distribution of tilt angles. The detail will be described elsewhere. The small peak located in the low-field region of the $H_\perp$ spectrum is assigned to disordered species.[29]

In contrast, the macrocycle plane of PM is almost perpendicular to the film surface in the LB film with hexatriacontane. The hyperfine splitting due to copper is clearly observed in the $H_\parallel$ spectrum, but not in the $H_\perp$ spectrum (Figure 1b). In the $H_\perp$ spectrum, the signal is almost a singlet with unresolved hyperfine structure. The $g$ value of this signal is ca. 2.05, which is similar to the $g_\perp$ value of the ordinary copper porphyrins.[27]

These results show that hexatriacontane molecules can control the orientation of PM molecules in the mixed LB film. The mechanism involved in this process is not clear at present. These phenomena may be relevant to the case in which a long-chain $n$-alkane such as octadecane has been used to fill the vacancy in the hydrophobic portion to form a densely packed monolayer when the hydrophilic part of the amphiphilic molecule is larger than its hydrophobic part.[32-35]

The amount of hexatriacontane can be very small to control the orientation of PM in the mixed LB films. The value $r = 0.5$ is sufficient to obtain the oriented spectra similar to the ones shown in Figure 1b. This value corresponds to the 3/1 mixing of porphyrin and hexatriacontane, suggesting the importance of molecular interaction. The change in the orientation is already recognized at the value $r = 0.1$.

The structure of the mixed LB film depends on the chain length of $n$-alkane added in the films. Similar phenomena, although to a much lesser extent, have been observed in the ESR spectra of mixed LB films containing octadecane, the length being half that of hexatriacontane, with the molar ratio up to $r = 2$.

In this communication, we have shown a new way to control the orientation of dye molecules in LB films without any chemical modification. To our knowledge, the present example is the first case where a distinct orientational change has been obtained by adding a small amount of a molecule, the "trigger molecule", if we may call it, in LB films. This method will provide a new strategy for the fabrication of LB films with aimed structures and functions.

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# Pure Absorption Gradient Enhanced Heteronuclear Single Quantum Correlation Spectroscopy with Improved Sensitivity

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Recent advances in pulsed field gradient technology have led to the incorporation of pulsed field gradients in a large number of high-resolution NMR experiments.[1-5] While the advantages of including pulsed field gradients in NMR experiments are well documented in the literature,[6-8] a disadvantage with many of the published applications is the generation of spectra having undesirable mixed mode line shapes. Recently, schemes for recording pure absorption heteronuclear correlation spectra where the amplitude of one of the gradient pulses changes in alternate $t_1$ points have been suggested.[9-11] Because either N- or P-type coherence pathways, but not both, are selected with each scan, the theoretical signal-to-noise (S/N) ratios of peaks in such spectra are down by a factor of $(2)^{1/2}$ relative to (nongradient) pure absorption spectra recorded in the same amount of measuring time. In this communication, we describe a pulse sequence for recording pure absorption $^1$H–$^{15}$N heteronuclear single quantum correlation (HSQC) spectra with coherence transfer selection achieved using gradients. This new method can offer sensitivity gains relative

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