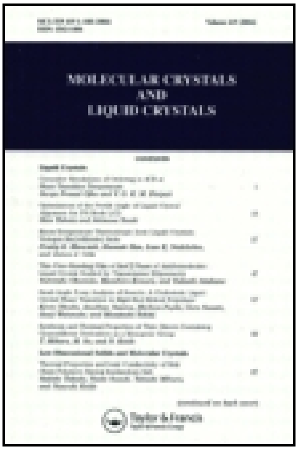

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Surface-Enhanced Raman Scattering of Charge Transfer Thin Films of Tetracyanoquinodimethane Derivatives on Metal Surface

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Surface-Enhanced Raman Scattering of Charge Transfer Thin Films of Tetracyanoquinodimethane Derivatives on Metal Surface

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The 488.0 and 1064 nm-excited Raman spectra have been measured for dipping films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ) and docosylpyridinum-TCNQ salt and mixed-stack charge transfer films of octadecyl-TCNQ doped with 3,3′,5,5′-tetramethylbenzidine (TMB) deposited on silver mirror. The 488 nm-excited Raman and 1064-nm excited FT-Raman spectra of dipping films of octadecyl-TCNQ and docosylpyridinum-TCNQ salt and CT film of octadecyl-TCNQ doped with TMB on the silver mirror gave very intense Raman bands with a high signal-to-noise ratio owing to the SERS effect. From the frequency of a C≡N stretching band of the CT film of octadecyl-TCNQ doped with TMB on silver mirror, the degree of CT can be calculated to be 0.42, suggesting that the CT film is in a quasi-neutral state. The C≡N stretching band of the dipping film of docosylpyridinium-TCNQ salt indicates the strong interaction of TCNQ group with silver mirror surface.

Keywords: surface-enhanced Raman scattering; thin films; charge transfer; tetracyanoquinodimethane

INTRODUCTION

A number of Langmuir-Blodgett (LB) films having tetracyanoquinodimethane (TCNQ) chromophores have recently been investigated, aiming at novel conducting materials.[1] We have been studying the molecular orientation and structure of LB films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ) and mixed-stack charge transfer (CT) films consisting of octadecyl-TCNQ doped with 3,3',5,5'-tetramethylbenzidine (TMB) deposited on CaF_2 plates and Au-evaporated glass slides by means of FT-IR, FT-Raman and surface-enhanced Raman scattering (SERS).[2, 3] The Raman study for mixed-stack CT films consisting of octadecyl-TCNQ doped with TMB showed that the structure of octadecyl-TCNQ and TMB does not change significantly between CaF_2 plate and Au-evaporated glass slide substrates, but the interaction between the first layer and the substrate affects the mechanism of CT.[3]

The purpose of the present study is to investigate the structure of dipping films of octadecyl-TCNQ and docosylpyridinum-TCNQ salt and CT film of octadecyl-TCNQ doped with TMB on the silver mirror by SERS with visible and near infrared excitation. This SERS study may provide complementary information to the previous study on the molecular structure and orientation in the LB and CT films of octadecyl-TCNQ.

EXPERIMENTAL

Detailed procedures for preparing the silver mirror, dipping films of octadecyl-TCNQ and docosylpyridinum-TCNQ salt and CT film of octadecyl-TCNQ doped with TMB on the silver mirror were described previously.[2, 4] The 488 nm-excited Raman spectra were measured at a 4 cm^{-1} resolution with a JASCO NRS-2100 Raman system and liquid nitrogen-cooled CCD detector. The 1064 nm-excited FT-Raman spectra were obtained at a 4 cm^{-1} resolution with a Nicolet Magna Spectrometer 860 equipped with an InGaAs detector.

RESULTS AND DISCUSSION

The 488 nm-excited Raman spectra of a dipping film of octadecyl-TCNQ and of a CT film of octadecyl-TCNQ doped with TMB on silver mirror show very intense Raman bands with a high signal-to-noise ratio owing to the SERS effect as shown in Figure 1A (a) and (b), respectively. It is of note that bands of the dipping film of octadecyl-TCNQ at 2221, 1608, and 1447 cm^{-1} due to C≡N, C=C (ring), and C=C (wing) stretching modes, respectively, show a shift upon the formation of the CT film. The degree of charge-transfer (ρ), determined from the shift of the C≡N stretching band, is 0.42, suggesting that the CT film is in a quasi-neutral state. The ρ value is very close to those obtained in our previous IR and Raman studies.[2,3] The 1064 nm-excited Raman spectrum of a CT film of octadecyl-TCNQ doped with TMB on silver mirror also shows a marked SERS effect (Figure 1A (c)). It is suggested that the silver mirror method is a

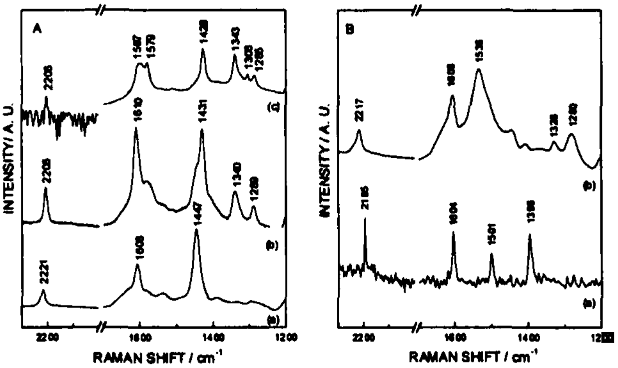

FIGURE 1 A. (a), (b); The 488 nm-excited Raman spectra of a dipping film of octadecyl-TCNQ (a) and of a CT film of octadecyl-TCNQ doped with TMB (b) on silver mirror. (c); The 1064 nm-excited FT-Raman spectrum of the CT film of octadecyl-TCNQ doped with TMB on silver mirror.
B. (a). The 1064 nm-excited Raman spectrum of the cast film of docosylpyridinium-TCNQ salt on CaF$_2$ plate. (b). The 488 nm-excited Raman spectrum of a dipping film of docosylpyridinium-TCNQ salt on silver mirror.

powerful method to obtain large SERS effect. It is noted that the 1064 nm-excited Raman spectra of the CT films on a gold evaporated glass slide and a CaF_2 plate which are pre-resonanced with a CT band near 1540 nm do not show strong Raman spectra like the SERS spectrum for the silver mirror.

Figure 1B shows (a) the 1064 nm-excited Raman spectrum of the cast film of docosylpyridinium-TCNQ salt on a CaF_2 plate and (b) the 488 nm-excited SERS spectra on silver mirror. From the comparison of the frequency of the $C\equiv N$ stretching mode of docosylpyridium-TCNQ salt between cast films on the CaF_2 plate and gold-evaporated glass slide (the spectra, not shown) and the dipping film on the silver mirror, it is suggested that the $TCNQ^-$ group interacts strongly with positive charged on the silver mirror surface.

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