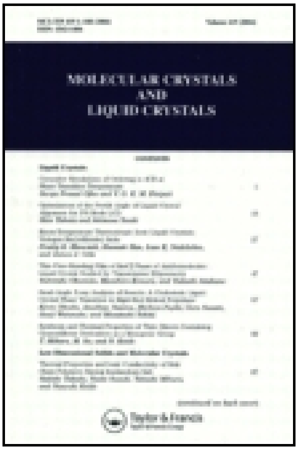

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# Raman Study of Mixed-Stack Charge Transfer Films of 2-Octadecyl-7,7,8,8-Tetracyanoquinodimethane and 3,3′,5,5′-Tetramethylbenzidine Prepared by the Langmuir-Blodgett Technique and Donor Doping

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# Raman Study of Mixed-Stack Charge Transfer Films of 2-Octadecyl-7,7,8,8-Tetracyanoquinodimethane and 3,3′,5,5′-Tetramethylbenzidine Prepared by the Langmuir-Blodgett Technique and Donor Doping

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Raman, FT-Raman and ultraviolet-visible-near infrared (UV-vis-NIR) spectra have been measured for mixed-stack charge transfer (CT) films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ) doped with 3,3',5,5'-tetramethylbenzidine (TMB) deposited on $CaF_2$ plates and Au-evaporated glass slides. The 1064 nm-excited FT-Raman spectra can be observed clearly even for the one-layer CT films deposited on $CaF_2$ plates because the excitation wavelength is located within a broad CT band centered near 1550 nm. The degree of the charge transfer determined by a shift of the C≡N stretching band of the TCNQ chromophore suggests that the CT complex films are in a quasi-neutral state.

*Keywords:* Langmure-Blodgett films; charge transfer; Raman spectroscopy; tetracyanoquinodimethane

## ITRODUCTION

Recently, great interest has been paid to mixed-stack organic charge-transfer (CT) complexes, composed of alternatively stacked donor (D) and acceptor (A) molecules because they show a variety of physical properties, such as nonlinear electrical and optical properties, and an anomalous dielectric response[1]. It is also notable that a neutral to ionic phase transition induced by pressure or temperature is observed for a number of mixed-stack CT complex crystals.

We have been studying the structure, morphology, and thermal behavior of the mixed-stack CT Langmur-Blodgett (LB) films consisting of octadecyl-TCNQ (A) and TMB (D) (Figure 1 a, b) by use of ultraviolet-visible-near infrared (UV-vis-NIR) and infrared (IR) spectroscopies and atomic force microscopy (AFM)[2,3]. The CT films we investigated show non-linear electrical conduction. The purpose of the present study is to provide a further insight into the structure and properties of the mixed-stack CT films of octadecyl-TCNQ doped with TMB by use of Raman and FT-Raman spectroscopy.

## EXPERIMENT

A detailed experimental procedure for preparing a LB film of octadecyl-TCNQ and the CT films was described previously[2]. The 488.0 nm-excited Raman spectra of the LB and CT films were measured at a 4 $cm^{-1}$ resolution with a Raman system consisting of a ARC Instruments SpectraPro 275 Triple Monochromator/Spectrograph and CCD detector (LN/CCD-1100PBUVAR, Priceton Instruments). The 488.0 nm line from an argon ion laser (Spectra-Physics 2016) was used as an excitation source for the Raman spectra. FT-Raman spectra were obtained at a 4 $cm^{-1}$ resolution with a Nicolet Magna Spectrometer 860 equipped with an InGaAs detector. UV-Vis-NIR spectra were measured with a Shimadzu UV-visible 3101 PC spectrophotometer.

## RESULTS AND DISCUSSION

Figure 1 A shows the 488.0 nm-excited Raman spectra of a 7-layer CT film of octadecyl-TCNQ doped with TMB (a) and a 7-layer LB film of octadecyl-TCNQ (b) both deposited on Au-evaporated glass slides. It is of note that bands at 2221, 1618, and 1461 $cm^{-1}$ due to C≡N, C=C (ring), C=C (wing) stretching modes, respectively, show a shift upon the formation of the CT film. The degree of charge-transfer ($\rho$) can be determined from the shift of the C≡N stretching band[4]. It was calculated to be 0.42, suggesting that the CT films are in a quasi-neutral state. The calculated value is very close to that obtained from our previous IR study [2].

Figure 1 B compares the 1064 nm-excited FT-Raman and 488 nm-excited Raman spectra of 7-layer CT films of octadecyl-TCNQ doped with TMB

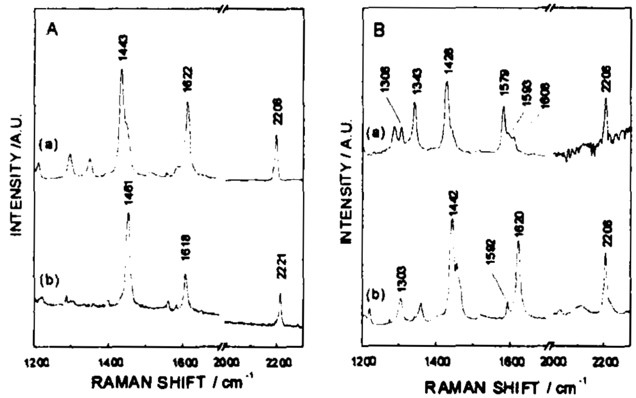

FIGURE 1 A. The 488 nm-excited Raman spectra of a 7-layer CT film of octadecyl-TCNQ doped with TMB (a) and a 7-layer LB film of octadecyl-TCNQ (b). B. The 1064 nm (a) and 488 nm-excited Raman (b) spectra of a 7-layer CT film of octadecyl-TCNQ and TMB deposited on a $CaF_2$ plate.

deposited on $CaF_2$ plates. An FT-Raman spectrum can be obtained even for a one-layer CT film of octadecyl-TCNQ and TMB (the spectrum, not shown). This is because the excitation wavelength is located within a broad band near 1550 nm assigned to a CT excitation between octadecyl-TCNQ (A) and TMB (D) molecules[2]. Thus, the 1064 nm-excited Raman spectra of the CT films are pre-resonance Raman spectra.

The excitation wavelength dependence of Raman spectrum of the 7-layer mixed-stack CT film can be observed in Figure 1 B. The spectral changes with the excitation wavelength arise from the fact that the 1064 nm-excited spectrum is pre-resonanced with the CT band near 1550 nm while the 488 nm-excited spectrum is pre-resonanced with a band due to an intramolecular excitation of TCNQ molecules. Of note is that bands assignable to TMB (1343 and 1608 $cm^{-1}$) are observed only in the 1064 nm-excited Raman spectra.

## Acknowledgments

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