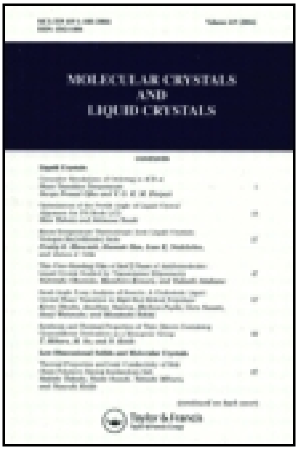

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AN INFRARED STUDY ON MOLECULAR ORIENTATION IN MIXED-STACK CHARGE TRANSFER FILMS OF 2-OCTADECYL-7,7,8,8-TETRACYANOQUINODIMETHANE AND 3,3',5,5'-TETRAMETHYLBENZIDINE PREPARED BY THE LANGMUIR-BLODGETT TECHNIQUE AND DONOR DOPING

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Abstract Molecular orientation in mixed-stack charge transfer (CT) films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (acceptor, *A*) doped with 3,3',5,5'-tetramethylbenzidine (donor, *D*) has been investigated by infrared (IR) transmission and reflection absorption (RA) spectroscopy. A comparison of relative intensities of IR bands originated from chromophores of *D* and *A* reveals that the long axes of both *D* and *A* are almost parallel to the substrate in a one-layer CT film. A layer dependence of the molecular orientation has been explored by a comparison of IR transmission and RA spectra of multilayer mixed-stack CT films.

INTRODUCTION

A mixed-stack organic charge-transfer (CT) complex, composed of alternatively stacked donor (*D*) and acceptor (*A*) molecules (• • • *DADADA* • • •), can be divided into two types, the so-called quasi-neutral (*N*) and quasi-ionic (*I*) states, according to the degree of CT between the *D* and *A* molecules. A neutral to ionic phase transition (NIT) induced by pressure or temperature has been observed for a number of mixed-stack CT complex crystals.[1] Their electric properties were also found to exhibit notable features at NIT, such as a remarkable increase in the electrical conductivity, an anomalous dielectric response and so forth.[2]

A systematic study on the structure, morphology and thermal behavior of the mixed-stack CT films consisting of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ, *A*) and 3,3',5,5'-tetramethylbenzidine (TMB, *D*) (Figure 1a,b), prepared by the

Langmuir-Blodgett (LB) technique and donor doping, has been carried out in our laboratory.[3,4] We aim at making novel low-dimensional functional materials with a controllable thickness by the molecular assembly technique. According to our previous atomic force microscopic (AFM) study, the mixed-stack CT films of octadecyl-TCNQ doped with TMB consist of one-dimensional needle-like microcrystals, in which the *D* and *A* molecules alternatively stack along the long axis of the microcrystals.[4] The *D-A* stacks were found to be preferentially oriented along the substrate surface by their polarized electronic spectra.[5] Furthermore, non-linear electrical conduction was observed for the CT films, although the non-linearity was weaker than that for a TMB-TCNQ crystal.[5] The purpose of the present study is to provide a further insight into the molecular orientation of *D* and *A* molecules in the CT films. Infrared (IR) transmission and reflection absorption spectroscopy (RA) has been employed.

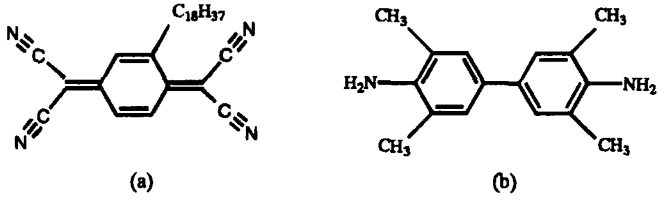

FIGURE 1 Structures of (a) 2-octadecyl-7,7,8,8-tetracyanoquinodimethane (octadecyl-TCNQ, *A*) and (b) 3,3',5,5'-tetramethylbenzidine (TMB, *D*).

EXPERIMENT

A detailed experimental procedure was described previously.[3]

RESULTS

Figure 2a,b shows IR transmission and RA spectra of one-layer mixed-stack CT films deposited on CaF_2 and Au substrates, respectively. Band assignments are not always straightforward due to the fact that the charge transfer between *D* and *A* makes a significant shift for a number of bands arising from *D* and *A* chromophores. In the RA spectrum (Figure 1b), 3496 and 3402 cm^{-1} are assigned to antisymmetric and symmetric stretching modes of NH_2 of TMB chromophore, respectively. These two bands are found to appear at 3404 and

3325 cm^{-1} for the neutral TMB molecule before the doping.[5] The upward shifts of about 100 cm^{-1} are caused by the chargee transfer between the *D* and *A* along the CT stacks. Since the directions of the transition moments of the antisymmetric and symmetric stretching bands are perpendicular and parallel to the long-axis of TMB molecule, respectively, the two bands can be used to evaluate the molecular orientation of the donor molecule. It can be observed that only the symmetric band at 3402 cm^{-1} shows an intense absorption in transmission spectrum (Figure 2a) while the antisymmetric one does not appear . In contrast, both the bands at 3496 and 3402 cm^{-1} are weak in the RA spectrum shown in Figure 2b. Thus, the long axes of the TMB molecules may be preferentially parallel to the substrate surface in the one-layer CT film.

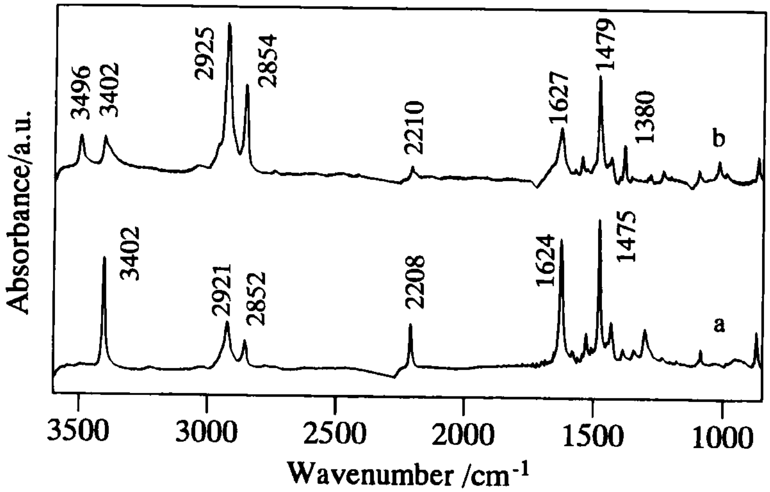

FIGURE 2 IR transmission (a) and reflection absorption (b) spectra of one-layer mixed-stack CT films of octadecyl-TCNQ and TMB.

In Figure 2, a band at 2208 cm^{-1} is assigned to the b_{1u} symmetric species of a $C\equiv N$ stretching mode in the octadecyl-TCNQ in a CT state. It vibrates along the long axis of the TCNQ chromophore, and thus is suitable for estimating the orientation of octadecyl-TCNQ. This band is much stronger in the transmission spectrum than that in the RA one revealing that the long axes of TCNQ chromophores are almost in parallel with the substrate. Two bands at 2921 and 2852 cm^{-1} are due to antisymmetric and symmetric CH_2 stretching modes of the hydrocarbon chain attached to the TCNQ chromophore. A comparison of the intensities of these two bands between the transmission and RA spectra enables one to investigate the orientation of the hydrocarbon chain. As they appear as weak and strong absorption bands in the transmission and RA spectra, respectively, the hydrocarbon chains seem to be preferentially parallel to the surface of the substrate.

IR transmission and RA spectra of seven-layer mixed-stack CT films were measured in order to study a layer dependence of the molecular orientation. The relative intensities of the bands at 2210 and 3402 cm^{-1}, assigned to the b_{1u} symmetric species of the C≡N stretching mode and NH_2 symmetric stretching mode, are stronger in the RA spectrum of the seven-layer CT film than that of the one-layer CT film. It implies that the long axes of both TCNQ and TMB chromophores are slightly more tilted to the substrate in the seven-layer CT film. A similar conclusion can also be obtained for the hydrocarbon chains from a comparison of the relative intensities of the CH_2 antisymmetric (2921 cm^{-1}) and symmetric (2852 cm^{-1}) stretching bands of the hydrocarbon chain for the one- and seven-layer CT films.

CONCLUSION

The present study, together with the previous investigations based upon AFM and polarized electronic spectra, has provided the following picture for the molecular arrangement, orientation, and structure in the mixed-stack CT films. The *D* and *A* molecules are alternatively stacked along the long axis of the one-dimensional needle-like microcrystals in which their planar chromophores are preferentially perpendicular to the substrates. The long axes of both *D* and *A*, including the hydrocarbon chains attached to *A*, are aligned almost parallel to each other and lie on the substrate surface for the one-layer CT film while they are slightly tilted in the multilayer CT films. This sort of alignment of *D* and *A* is advantageous to the charge transfer between *D* and *A* molecules.

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