

Optical Properties of Oriented Oligothiophene Thin Films

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1. Introduction

The carrier transport and luminescence properties of organic materials have attracted considerable attention. Fuji Electric has been working on the fundamental research of thin-film devices based on organic materials, due to their potential as future electronic and optoelectronic devices.

Conjugated polymers show unique optical and electronic properties including optical nonlinearity, carrier transport, and optical anisotropy. These properties are a result of the π -conjugated electrons delocalized in a one-dimensional polymer backbone. However, long-chain polymers have complex problems such as solubility, structural defects, and a broad distribution of chain length. Optical and electronic properties and the effective conjugation length reflect the disordered nature of polymers.

Recently, oligomers of short chain lengths have received much attention as model compounds to better understand the electronic and optical properties of polymers. This is because oligomers are well-defined chemical systems, and their conjugation chain length can be precisely controlled. Optical properties of linear oligomers, oligothiophene and thiophene-based oligomers in solution have been studied. However, there is little knowledge of the electronic properties of linearly-conjugated oligothiophenes in the solid phases, such as single crystals and thin films. This is a serious obstacle to the improvement of organic thin-film devices.

Since organic molecular semiconductors are formed from the assembly of molecules by weak van der Waals interactions, optical and electronic properties of solid states are determined by individual molecules and the spatial ordering of individual molecules. In order to produce high-quality, organic, thin-film devices, we need to arrange the molecules. We attempted to fabricate oriented thin films based on oligothiophene and thiophene-based oligomers. In this paper, we review recent experimental studies on the optical and structural properties of designed thiophene-based oligomers.

2. Control of Optical Properties

The structures of oligothiophenes (T_n , where n is the number of thiophene rings and $2 \leq n \leq 6$) are shown in Fig. 1. Their electronic structures are roughly considered a "short polyene" in which the conjugated c - c double bonds are locked in a plane and weakly perturbed by sulfur atoms.

Figure 2 shows absorption and normalized photoluminescence (PL) spectra of T_n . With an increase in the chain length of T_n , a shift of the absorption and PL peaks to longer wavelengths is observed. The height of the absorption peak of the lowest excitation state also increases with increasing chain length. Oscillator strength of the lowest excitation state, which is calculated from the integration of the lowest absorption band, increases linearly with conjugation length. The effective conjugation length of T_n is estimated at six or more thiophene rings. The bandwidth of the lowest absorption spectrum narrows with increasing chain length. This result implies that the narrow absorption band in T_n with the longer chains is due to the electrons delocalized in the one-dimensional backbone chain.

Figure 3 shows the lowest peak energy in the absorption spectrum (E_{ABS}) and the highest peak energy in the PL spectrum (E_{PL}) as a function of the number of

Fig.1 Chemical structures of oligothiophenes (T_n) and thiophene-based oligomers (T_nMT_n , T_nPT_n , and T_nVT_n)

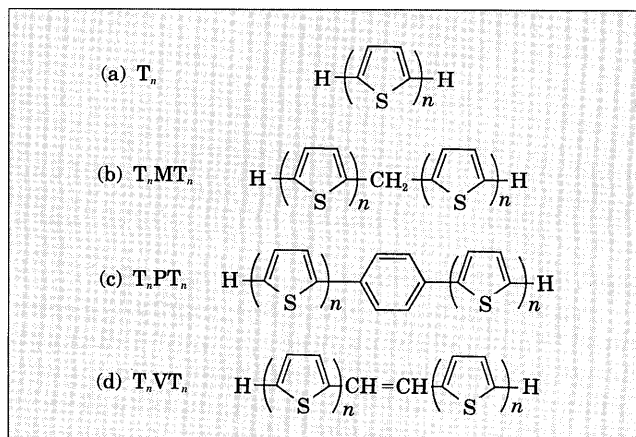


Fig.2 Optical absorption and PL spectra of T_n ($n=2$ to 5)

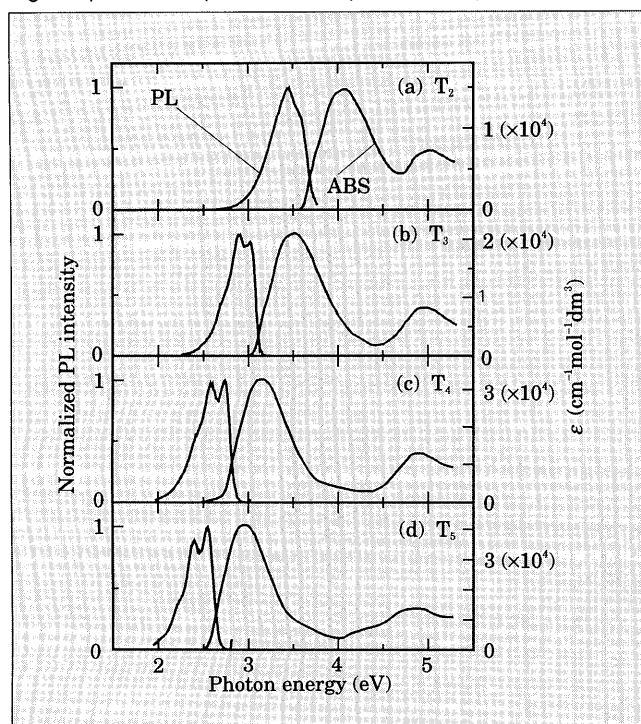
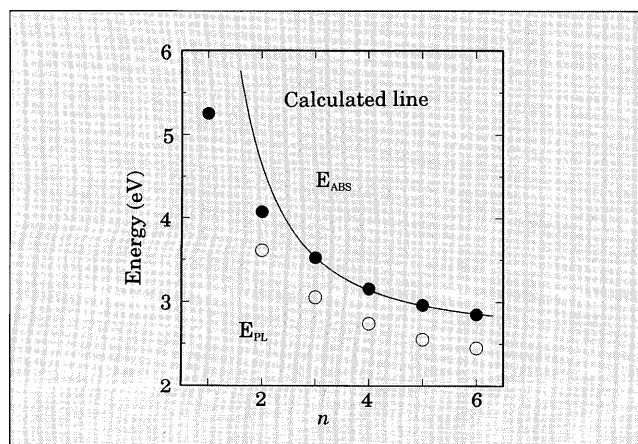


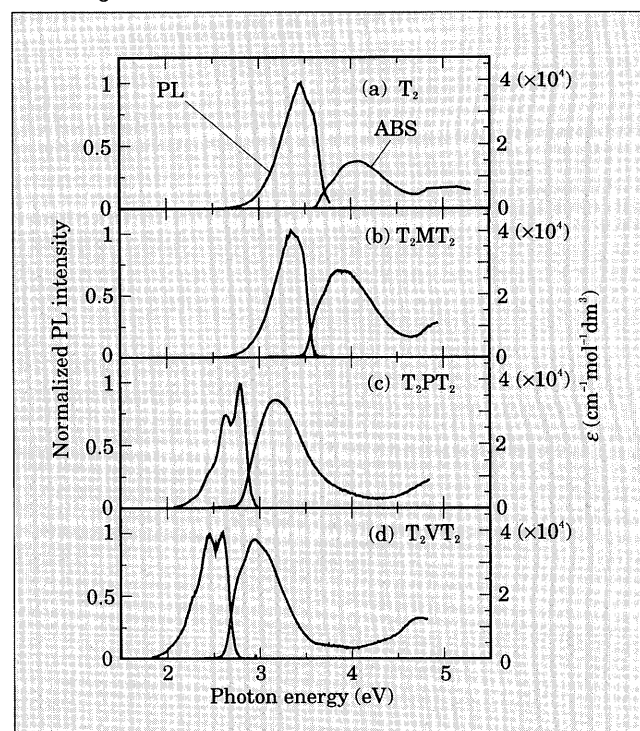
Fig.3 The lowest absorption peak energy (E_{ABS}) and the highest PL peak energy (E_{PL}) in oligothiophenes as functions of the number of thiophene rings, n (backbone chain length)



thiophene rings (n). The solid line is calculated from a simple one-dimensional quantum-well model. The confinement potential for the lowest excitation state is assumed to be infinite. In spite of the simplicity of this model, the calculated line corresponds with the observed values of E_{ABS} . The value of E_{ABS} ($n \rightarrow \infty$) agrees with $E_{\text{ABS}} = 2.6$ eV in the electrochemically polymerized polythiophene. These results indicate that the blue-shift of the lowest absorption peak is nearly due to the quantum confinement effect of electrons in the quasi-one-dimensional backbone.

We have designed the following organic, quasi-one-dimensional heterostructures: thiophene-based oligomers with methylene ($T_n\text{MT}_n$), phenylene ($T_n\text{PT}_n$), and

Fig.4 Optical absorption and PL spectra of thiophene-based oligomers T_2 , $T_2\text{MT}_2$, $T_2\text{PT}_2$, and $T_2\text{VT}_2$



vinylene ($T_n\text{VT}_n$) bridges. These structures are shown in Fig. 1.

Figure 4 shows absorption and PL spectra of oligothiophenes (T_2) and thiophene-based oligomers ($T_2\text{MT}_2$, $T_2\text{PT}_2$, and $T_2\text{VT}_2$). In these oligomers, the well structure is bithiophene and the barrier structures are methylene, phenylene, and vinylene, whose energy gaps are larger than that of bithiophene. Both absorption and PL spectra vary with the barrier structures. The peak energy of $T_2\text{PT}_2$ and $T_2\text{VT}_2$ shifts to lower energy, compared with that of T_2 and $T_2\text{MT}_2$. The π -conjugated electrons in $T_2\text{PT}_2$ and $T_2\text{VT}_2$ are extended over these oligomers, and their absorption and PL spectra are similar to those of T_4 or T_5 . Only methylene effectively acts as a barrier (the electrons are confined to the bithiophene). The electronic properties of the well-barrier-well structures based on these oligomers are not controlled by the energy-gap difference between only two constituent materials but are strongly affected by the delocalized nature of the electrons or the excitons.⁽¹⁾

3. Fabrication of Oriented Thin Films

Figure 5 shows optical absorption and PL spectra of T_4 in CH_2Cl_2 solution, T_4 doped in a polymethylmethacrylate (PMMA) matrix, and vacuum-evaporated T_4 crystalline film all at room temperature. Isolated T_4 molecules exhibit broad absorption and PL bands. The lowest absorption band is due to the π - π^* transition along the polyene backbone chain. In crystalline thin films, two absorption peaks appear near the lowest

Fig.5 Optical absorption and PL spectra of T_4 molecules at room temperature

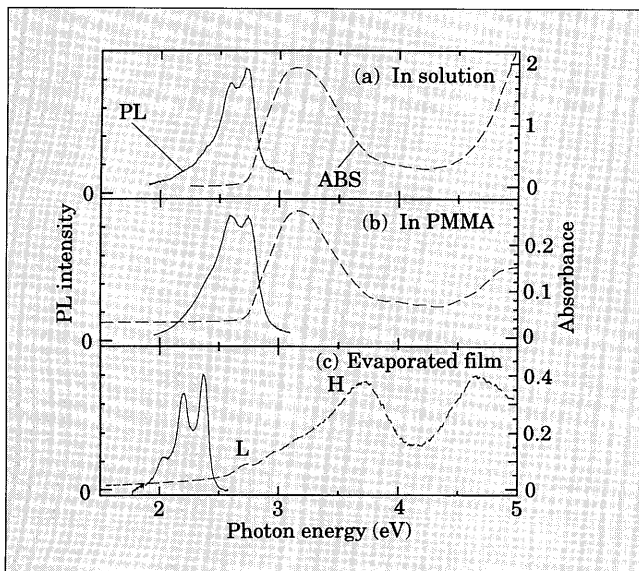
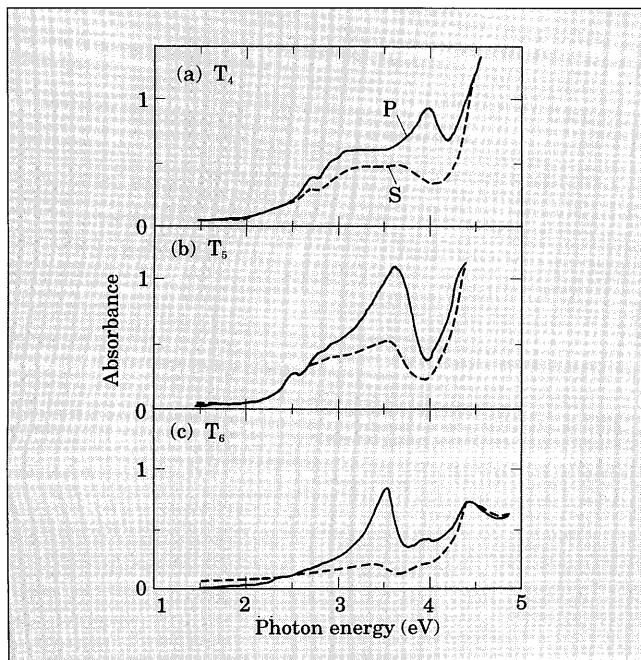


Fig.6 Absorption spectra with the polarized light of T_n ($n=4$ to 6) thin films



absorption band of the isolated molecules. A weak lower-energy band (denoted as the L band in Fig. 5 (c)) and a strong higher-energy band are also observed. It is thought that in crystalline films, the lowest absorption band of isolated molecules is split into two.

Figure 6 shows absorption spectra of crystalline T_4 , T_5 , and T_6 films. At an oblique angle (45°), these absorption spectra of the thin films were measured by polarizing the light parallel (p-polarization) and perpendicular (s-polarization) to the incident plane using the Glan-Thomson calcite prisms shown in Fig. 7. The sharp and blue-shifted H-absorption band is also observed in crystalline T_5 and T_6 films. The thickness of the T_4 and T_5

Fig.7 Measurement system of absorption spectra with the polarized light

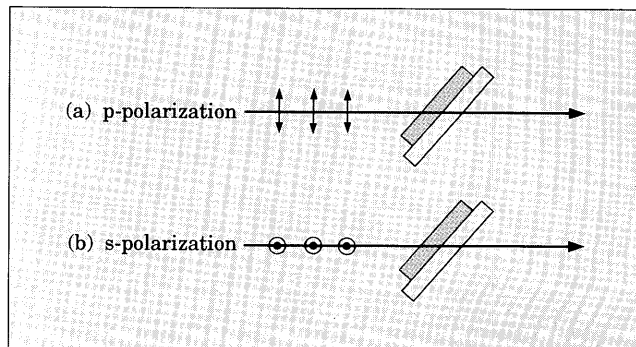
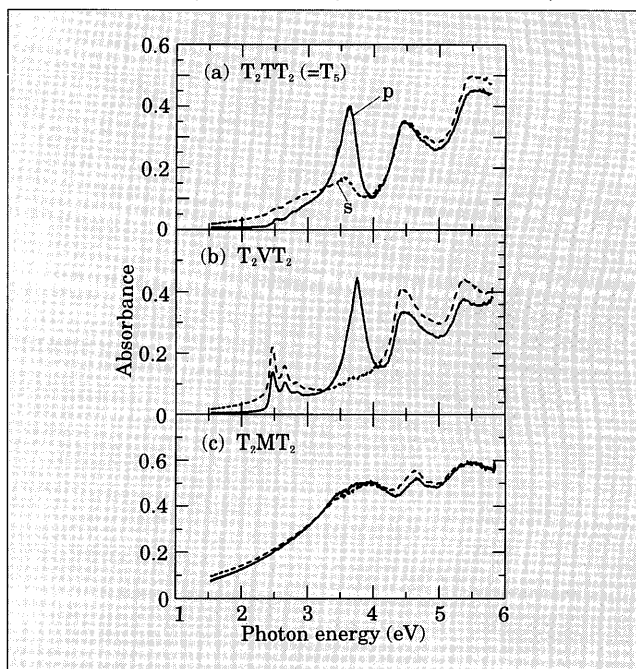


Fig.8 Absorption spectra with polarized light of vacuum-evaporated films (T_5 , T_2VT_2 , and T_2MT_2)

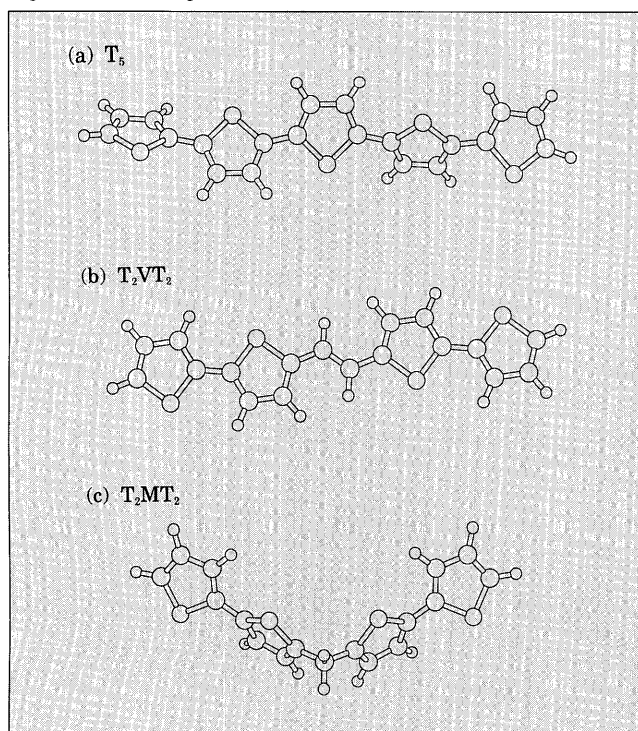


films was 250nm and the T_6 film was 200nm. The deposition rate of the T_4 and T_5 films was 50nm/min, and the T_6 film was deposited at 0.05nm/min.

The behavior of the H bands in all three crystalline films was similar. The absorbance of these H bands was clearly observed when using obliquely p-polarized light. This result indicates that the dipole moment is aligned normal to the surface in these films. Since the transition dipole moment in these films should be aligned along the molecular long axis, the long axis is confirmed to be aligned normal to the surface.⁽²⁾ Anisotropic absorption spectra were seen only in T_6 films with a slow deposition rate of 0.05nm/min but not observed in T_6 films with a high deposition rate of 50nm/min. The absorption spectra of crystalline films depend on the film fabrication conditions. Therefore, the molecular orientation of oligomers with a longer chain length is very sensitive to deposition rate.^(3,4)

Figure 8 shows optical absorption and PL spectra of the vacuum-evaporated crystalline films T_5 , T_2VT_2 , and

Fig.9 Calculated geometries of T_5 , T_2VT_2 , and T_2MT_2 molecules



T_2MT_2 . The thickness of these films was 50nm. In T_5 and T_2VT_2 films, optical density with p-polarized light (solid line) is larger than that with s-polarized light (broken line). Absorption spectra did not show anisotropy at the normal incidence for each sample. These results indicate that in the crystalline T_5 and T_2VT_2 films, the quasi-one-dimensional, molecular long axis is aligned along the surface normal. However, in T_2MT_2 films, the dichroism of the absorption spectrum is not observed. Sharp absorption bands are also not observed. The peak energy of the PL spectrum in the T_2MT_2 films is close to that of the isolated molecules in solution. Molecular orientation does not occur in T_2MT_2 films. These results suggest that modification of the chemical structures of individual molecules and oligomers affects the spatial arrangement of the molecules in crystalline films.

To understand why T_2VT_2 films are highly oriented crystalline ones but T_2MT_2 films are disordered ones, we calculated the stable geometry of isolated oligomers using the semiempirical PM3 molecular orbital calculation method. All calculations were performed using ver. 6.0 of the MOPAC program (QCPE#455). Introduction of the barriers into the conjugated backbone chain changes the molecular geometry and chain flexibility.⁽¹⁾ The calculated stable geometries of these molecules are shown in Fig. 9. The T_2MT_2 molecule has a bent structure. The bent oligomers are not favorable for the growth of oriented crystalline films because of the difficulty in stacking closely the molecules during deposition. The T_5 molecule has a twisted structure but not a

planar structure. The T_2VT_2 molecule has a planar structure. We speculate that planar molecules are easily piled up in the close packing form, compared to bent or twisted molecules. Under our experimental conditions (a relatively high deposition rate of 50 nm/min and a low substrate temperature of 25°C), planar and rigid oligomers are suitable for the formation of oriented crystalline films. The introduction of bridge structures between thiophene rings affects the spatial orientation in films as well as the electronic properties of isolated molecules. Further experimental and theoretical studies are needed to understand the detailed correlation between the optical and structural properties of thiophene-based oligomer crystalline films.

4. Conclusion

In this paper, we reported a new approach to designing optical and structural properties of thiophene-based oligomers having the well-barrier-well structures in quasi-one-dimensional backbone chains. The electronic properties of the well-barrier-well structures based on the oligomers are strongly affected by the delocalized nature of the electrons or the excitons.

We have demonstrated that highly oriented, organic thin films can be fabricated by improving the evaporated condition and introducing molecular heterostructures consisting of well and barrier parts. In particular, the molecular design of semiconductor heterostructures produces high-quality, organic, thin-film devices with improved electrical and optical characteristics.

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