PHYSICAL REVIEW B VOLUME 50, NUMBER 4 15 JULY 1994-II

Optical properties of quasi-one-dimensional thiophene-based oligomers

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(Received 16 February 1994)

We have studied optical properties of one-dimensional oligothiophenes and thiophene-based oligomers. The thiophene-based oligomers have the well-barrier-well structures in quasi-one-dimensional backbone chains, where the well parts are the oligothiophenes with different conjugation lengths and the barrier parts are nonvisibly luminescent materials with larger energy gaps. The chain-length dependence of the optical properties of oligothiophenes shows that excitons are localized within two thiophene rings and the luminescence decay is controlled by the diffusion of localized excitons. Furthermore, luminescence properties of thiophene-based oligomers such as luminescence yield, luminescence lifetime, and luminescence wavelength can be controlled by changing the conjugation length of the well part and the barrier structure. Spectroscopic analysis and molecular-orbital calculations show that the exciton localization and radiative recombination processes are affected by the rotational motion of thiophene rings.

I. INTRODUCTION

Quasi-one-dimensional semiconductors, often called quantum wires, have attracted considerable attention because they exhibit a wealth of quantum phenomena and have a potential as future optoelectronic devices.[1] Chemically synthesized semiconducting polymers are regarded as natural quantum wires.[2] Polythiophene is a prototype of conjugated polymers having a nondegenerate ground-state structure: Its electronic structure is approximately considered as a polyene in which the conjugated $C=C$ double bonds are locked in plane. Unique optical and electronic properties of polythiophene are due to the π-conjugated electrons delocalized one-dimensional polymer backbone, and they make it an important material for technological applications such as light-emitting diodes,[3] nonlinear optical devices,[4] field-effect transistors,[5] and so on. However, long-chain polythiophenes have the complexity of the "real" polymer such as solubility, structural defects, the broad distribution of the chain length, etc. Optical and electronic properties reflect this disorder nature of polymers. The effective conjugated length and disorders of polymers also depend on the polymer film fabrication method.

Recently, oligomers of short chain lengths have received much attention as model compounds for a better understanding of the electronic and optical properties of polymers.[6] Oligomers are well-defined chemical systems: The conjugation chain length can be exactly controlled. Studies of the size dependence of optical and electronic properties of oligomers with well-defined lengths help to check theoretical predictions[7] and to understand the microscopic mechanism of radiative and nonradiative recombination processes.[8]

In this paper, we report the size dependence of optical properties in oligothiophenes in solutions. The excitons are spatially localized within two thiophene rings, and the luminescence decay time is limited by the exciton diffusion to the chain end of a nonradiative recombination center. We synthesized a family of thiophene-based oligomers in order to control the optical properties and the backbone rigidity of oligomers. Spectroscopic analysis and molecular-orbital calculations suggest that the exciton localization and radiative recombination processes are affected by the rotational motion of thiophene rings.

II. EXPERIMENT

The structures of oligothiophenes (T_n, where n is the number of thiophene ring, $2 \leq n \leq 6$) and thiophene-based oligomers with methylene (T_nMT_n), phenylene (T_nPT_n), and vinylene (T_nVT_n) bridges are shown in Fig. 1. The details of synthesis and purification methods of T_n,[9-11] T_nMT_n,[12,13] T_nPT_n,[13,14] and T_nVT_n (Ref. 15) are described in the literature.

Optical absorption and photoluminescence (PL) spectra were measured in CH_2Cl_2 solutions

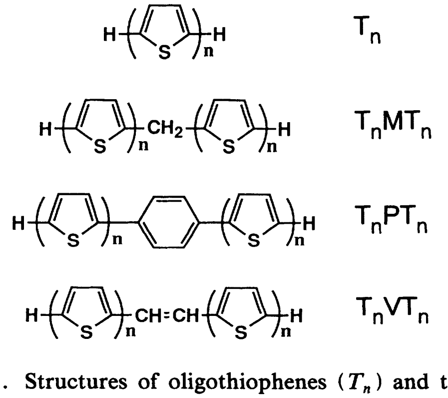

FIG. 1. Structures of oligothiophenes (T_n) and thiophene-based oligomers (T_nMT_n, T_nPT_n, and T_nVT_n).

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(1.0×10^{-5} mol/dm^3). The PL spectra were measured using a 325-nm excitation light from a He-Cd laser. The calibration for the spectral sensitivity of the entire measuring system was performed by using a tungsten standard lamp.

Picosecond PL decay measurements were carried out by using a dye laser (310 nm) with 1-ps pulse duration and a double monochromator of subtractive dispersion and a synchroscan streak camera. The temporal resolution of this system was about 30 ps.

III. RESULTS AND DISCUSSION

A. Oligothiophenes

Figure 2 shows absorption and normalized PL spectra of oligothiophenes T_n. With an increase of 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. The oscillator strength of the lowest excitation state, which is calculated from the integration of the lowest absorption band, linearly increases with the conjugation length. The effective conjugation length of oligothiophenes is estimated to be six thiophene rings or more. The bandwidth of the lowest absorption spectrum becomes narrow with increasing chain length. This result implies that the sharp absorption band in oligothiophenes with longer chains is due to the electrons delocalized in the one-dimensional backbone chain.[1]

Figure 3 shows the lowest peak energy in the absorption spectrum, E_L, as a function of the number n of the thiophene ring. The energy level of the lowest state is calculated from a simple one-dimensional quantum-well model. The finite confinement potential for the lowest excitation state V_0 is assumed to be $V_0 = E_S - E_g$, where E_S is the lowest absorption peak energy of the CH$_2$Cl$_2$ solvent and E_g is the lowest absorption energy of polythiophene ($n \rightarrow \infty$). The solid line is a calculated one with $E_S = 7$ eV and $E_g = 2.4$ eV in the electrochemically polymerized polythiophene reported in Ref. 16. The calculated results agree well with the observed values of E_L. This indicates that the blueshift of the lowest absorption peak energy is due to the quantum confinement effect of electrons in the quasi-one-dimensional backbone.

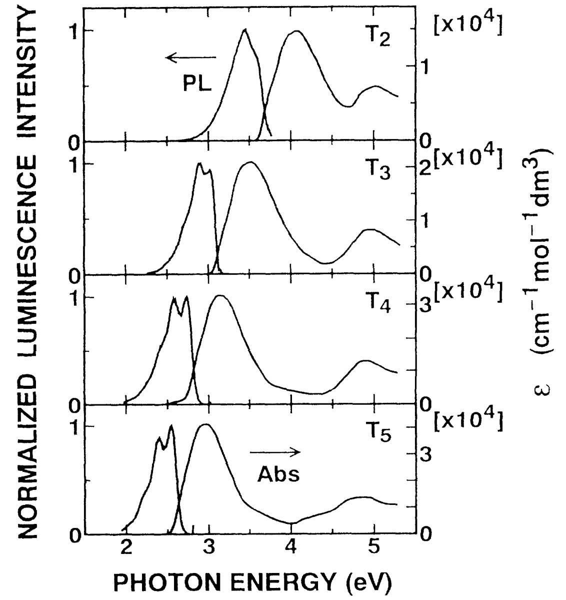

FIG. 2. Optical absorption and photoluminescence spectra of T_n ($n = 2$–5). The peak energies of the absorption and PL spectra shift to lower energy with increasing chain length.

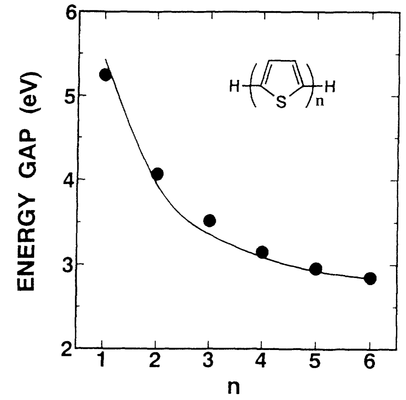

FIG. 3. The lowest absorption peak energy in oligothiophenes as a function of the number of the thiophene ring (backbone chain length.) The calculated energy gap of T_n from a simple quantum well model is given by the solid line.

Time-resolved luminescence spectra of T_n in the picosecond time region are shown in Fig. 4. The PL decay curves at the PL peak energy are approximately given by single exponential functions. The PL lifetime τ_{PL} increases with increasing chain length. In Fig. 5, the size dependence of the PL lifetime and the PL quantum yields η are summarized. The PL quantum yields η were deter-

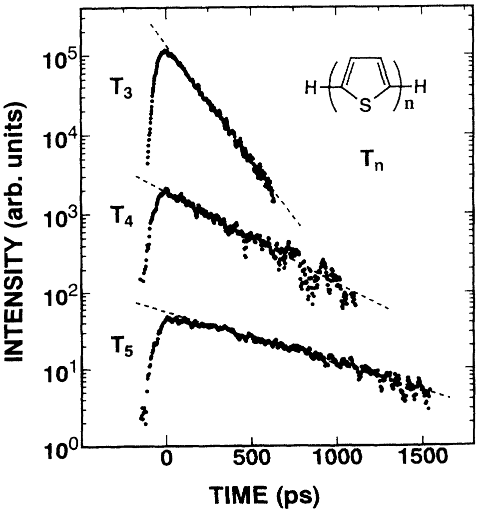

FIG. 4. Picosecond photoluminescence decay profiles in oligothiophenes T_n. The decay curves are given by the single exponential function. The PL lifetime increases with increasing chain length.

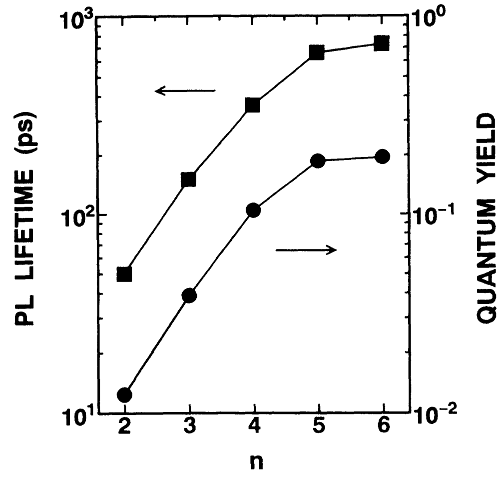

FIG. 5. Chain length dependence of the PL lifetime and PL quantum yield in T_n. The chain length dependence of the PL lifetime is very similar to that of the PL quantum yield.

mined by using quinine sulfate as a standard material.[17] Both the lifetime and the quantum yield increase with increasing chain length. The similar size dependence of τ_{PL} and η implies that the observed PL lifetime is limited by the nonradiative recombination process, and that the nonradiative decay rate decreases with increasing chain length.

Here we assume that the PL decay rate τ_{PL}^{-1} is determined by two relaxation channels having the radiative decay rate τ_R^{-1} and the nonradiative decay rate τ_{NR}^{-1} ($\tau_{PL}^{-1}=\tau_R^{-1}+\tau_{NR}^{-1}$). The PL quantum yield η is given by $\tau_R^{-1}/(\tau_R^{-1}+\tau_{NR}^{-1})$ and then τ_R is τ_{PL}/η. The chain-length dependence of the estimated radiative lifetime τ_R is summarized in Fig. 6. Since both the PL lifetime and the PL quantum yield increase with increasing chain length, the radiative lifetime does not depend on the chain length. In all oligothiophenes, the radiative lifetime is about 4 ns. Therefore, we need to consider the size-independent radiative recombination process. A possible model is that the excitons are spatially localized within two thiophene rings, and PL originates from the radiative recombination of localized excitons. The recombination process will be also discussed in Sec. III B.

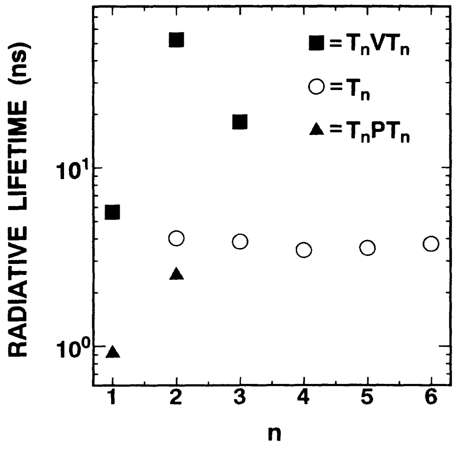

FIG. 6. Radiative lifetime as a function of the chain length. The radiative recombination rate does not depend on the chain length in T_n. This implies that the exciton is strongly localized within two thiophene rings. The radiative lifetimes in thiophene-based oligomers, T_nPT_n and T_nVT_n are also shown in this figure.

On the other hand, Fig. 5 also indicates that both the efficiency of the nonradiative recombination and the nonradiative decay rate decrease with increasing chain length. Here we assume that the end of the chain acts as a nonradiative recombination center, and that the exciton migration toward a nonradiative recombination center can be described by the one-dimensional random walks of a neutral particle on a finite chain.[18] The survival probability of excitons at long time t, $S(t)$, is given approximately by[18]

$$S(t)=\frac{8}{\pi^2}\exp\left[-\frac{\pi^2Dt}{L^2}\right], \tag{1}$$

where D is the diffusion constant, and L is the conjugation length. In this model, the PL decay time is determined by the exciton diffusion process, and the PL decay profile is exponential with a time constant of $\tau_{PL}=L^2/\pi^2D$. Figure 7 shows the size dependence of τ_{PL} as a function of the square of the number of thiophene rings, n^2, where the chain length L is given by $L=0.56n$ (nm). A linear relationship is observed, and the slope gives the diffusion coefficient of about 1.5×10^{-5} cm^2/s, which is small compared with that in an electrochemically polymerized polythiophene.[19] We believe that the difference of the diffusion constant between oligomers and polymers is mainly caused by the difference of the sample structure between the solution and solid films and the difference of the stiffening of the chains between oligomers and polymers. Although the chain length is short ($n=2-6$), this figure strongly suggests that the nonradiative recombination occurs at the end of the chain, and the PL lifetime is controlled by the diffusion of excitons to the chain end.

B. Thiophene-based oligomers

Figure 8 shows absorption and photoluminescence spectra of oligothiophenes and thiophene-based oligomers, T_2, T_2MT_2, T_2PT_2, and T_2VT_2. In these oligomers, the well part is bithiophene, and the barrier part is methylene, phenylene, and vinylene, whose energy gaps are larger than that of bithiophene. Both absorption and luminescence spectra vary with the *barrier* structure. The peak energy of T_2PT_2 and T_2VT_2 shifts to lower energy, compared with that of T_2 and T_2MT_2. The π-conjugated electrons in T_2PT_2 and T_2VT_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 conjugated polymers and oligomers are not controlled by the energy-gap difference between two constituent materials only, and are strongly affected by the delocalization nature of the electrons or the excitons.

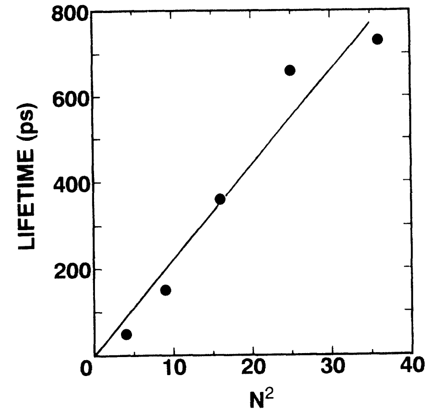

FIG. 7. Photoluminescence decay time as a function of the square of the chain length. A linear relation suggests that the chain end acts as a nonradiative recombination center, and the nonradiative recombination rate is limited by the exciton diffusion to the chain end.

Picosecond PL decay profiles in T_nMT_n, T_nPT_n, and T_nVT_n were also given by a single-exponential function. However, the PL lifetime and the PL quantum yield strongly depend on the *barrier* kind of thiophene-based oligomers. The size dependence of the radiative lifetime in T_n, T_nPT_n, and T_nVT_n is also summarized in Fig. 6. In these materials, the τ_R ordering is $T_nPT_n < T_n < T_nVT_n$ and the η ordering is $T_nVT_n < T_n < T_nPT_n$. The dynamics of PL decay, the PL peak energy, and the PL quantum yield can be controlled by the kind of the barriers in thiophene-based oligomers.

As mentioned above, the radiative decay rate in oligothiophenes T_n does not depend on the number of the thiophene ring. On the other hand, the radiative decay rate in thiophene-based oligomers depends on the structure of the barrier part. To understand the PL process in thiophene-based materials, we consider the effect of the rotational motion of thiophene rings on the radiative recombination process in oligothiophenes and thiophene-based oligomers, because the introduction of the barrier part into the polymer backbone changes the backbone rigidity (or chain flexibility). Rotational barriers of the thiophene rings around the interring bond were calculated for T_3, T_1PT_1 and T_1VT_1 using the semiempirical PM3 molecular-orbital calculation method.[20] All calculations were done by using MOPAC ver. 6.0 program (QCPE#455). Figure 9 shows the PM3 potential curves as a function of the torsion angle between the thiophene rings. The rotational barrier-height ordering is $T_1VT_1 > T_3 > T_1PT_1$. The radiative lifetime and the PL quantum yield are related to the rotational barrier height: The well-barrier-well structures having lower rotational barrier exhibit high PL efficiency and fast radiative decay rate. These results show that rotational motion plays an important role in the radiative process. The rotational motion of thiophene rings enhances the localization of the exciton, causing both a higher PL efficiency and a faster radiative decay. Our results for thiophene-based oligomers suggest that the rotational defect is a radiative recombination center in polythiophene solid films.[21]

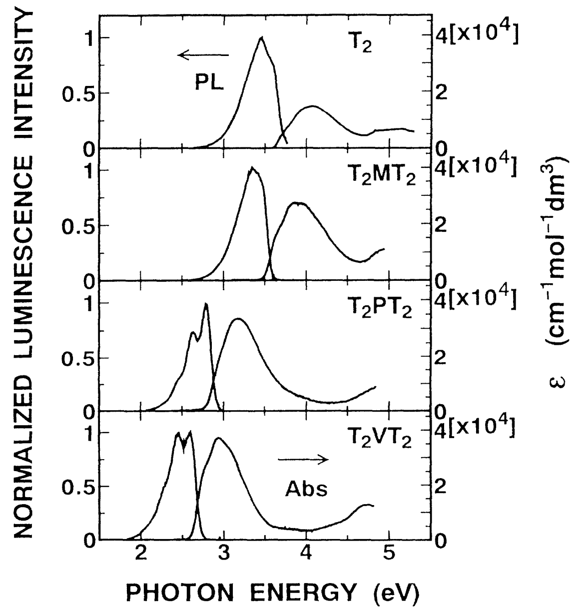

FIG. 8. Optical-absorption and photoluminescence spectra of thiophene-based oligomers, T_2, T_2MT_2, T_2PT_2, and T_2VT_2. The well part in these structures is bithiophene.

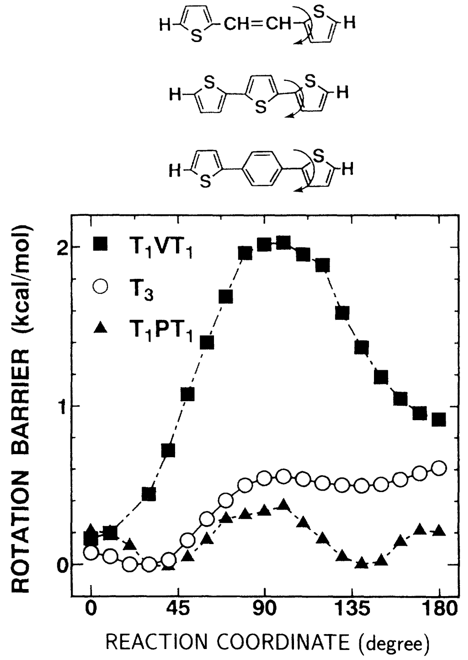

FIG. 9. PM3 potential curves as a function of the torsion angle between the thiophene rings. The vertical axis represents the heat of formation in the PM3 method.

IV. CONCLUSIONS

We have studied optical properties of oligothiophenes and thiophene-based oligomers. The size dependence of the optical properties of oligothiophenes indicates that the excitons are spatially localized within two thiophene rings, and the luminescence decay time is limited by the exciton diffusion to the chain end of a nonradiative recombination center. Moreover, spectroscopic analysis and molecular-orbital calculations suggest that the exciton localization and radiative recombination processes are affected by the rotational motion of thiophene rings. Luminescence properties of quasi-one-dimensional thiophene-based oligomers such as luminescence yield, luminescence lifetime, and luminescence wavelength can be controlled by changing the conjugation length of the well part and the barrier structure. The polymeric heterostructures consisting of the well part emitting the light and the barrier part controlling the chain rigidity (the solubility and film-forming properties of the polymers) become unique soluble light-emitting materials.

ACKNOWLEDGMENTS

One of the authors (Y.K.) thanks to Dr. S. Abe of Electrotechnical Laboratory for useful discussions and the Iketani Science foundation for financial support.

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