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Third-harmonic generation in CT-type conjugated polymers

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We have studied the nonlinear optical properties of a conjugated copolymer, poly(2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl) (PThQx), in which thiophene (Th) and quinoxaline (Qx) molecules are arranged alternately and act as donors and acceptors, respectively. The optical gap of PThQx corresponds to the charge-transfer (CT) excitation from Th to Qx. In order to clarify the third-order optical nonlinearity, we have performed the third-harmonic generation (THG) measurements on a spin-cast thin film of PThQx. The third-order nonlinear susceptibility ($\chi^{(3)}$) evaluated by the THG measurements reaches to 2×10^{-11} esu at the three-photon resonance to the CT excited state. This value is comparable to that of head-to-tail poly(3-hexylthiophenes) (PTh), though PThQx shows smaller absorption coefficient (α) around the optical gap. Such a feature of PThQx can be explained by considering the CT character of the excited states. The small α and the large $\chi^{(3)}$ value in PThQx lead to a large figure of merit in nonlinear optical response. The results indicate that CT-type conjugated copolymer would be a good candidate of third-order nonlinear optical materials.

Key words: CT-type conjugated polymer, third-order optical nonlinearity, third-harmonic generation

1. INTRODUCTION

The control of optical gap energies in organic materials is an important subject to achieve organic optoelectronic devices such as electroluminescent devices and nonlinear optical devices. In conjugated polymers, a main approach to this subject has been the development of the constituent monomers as well as the control of the conjugation length. On the other hand, in organic charge-transfer (CT) complexes, the control of the optical gap energies is achieved by the choice of the donor and acceptor molecules [1]. Recently, this strategy for the CT complexes has been applied to the conjugated polymers [2]. The conjugated copolymers consisting of donors with small ionization potential and acceptors with large electron affinity are synthesized. In such copolymers, the optical gap corresponds to the CT excitation between donors and acceptors, and the control of the optical gap energies has been successfully made. For a new type of conjugated polymers, PThQx, we have measured the third-order nonlinear susceptibility ($\chi^{(3)}$) spectrum by using the third-harmonic generation (THG) method. From the comparison with a normal conjugated polymer, PTh, we will discuss the nature of the electronic states of CT-type conjugated copolymers governing the third-order nonlinear optical processes.

2. EXPERIMENTAL

2.1 Sample preparation

A copolymer consisting of thiophene (Th) and quinoxaline (Qx), poly(2,3-bis-(3-octyloxyphenyl) quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl) (PThQx), is synthesized from two monomers, 2,5-bis(trimethylstannyl)thiophene and 2,3-bis(3-octyloxy-phenyl)-5,8-dibromoquinoxaline by organometallic

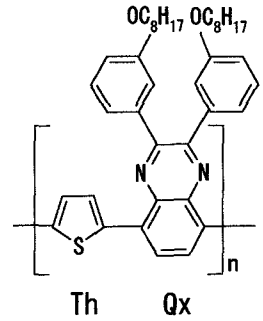

Fig. 1 Th-Qx copolymer

reaction. The synthetic method was reported in detail previously [2,3]. The chemical structure of PThQx is shown in Fig. 1. The copolymer can be dissolved into organic solvents such as $CHCl_3$ and toluene. For optical measurements, we fabricated a spin-cast film of PThQx from the $CHCl_3$ solution onto SiO_2 substrates.

2.2 Optical measurements

All optical measurements are done at room temperature. Absorption spectra are measured by the spectrometer JASCO MSV-370. In the luminescence measurements, we use a tunable femtosecond laser (pulse width ~100fs) as an excitation light source. The luminescence spectra were measured by using a streak camera (Hamamatsu photonics C4334). In THG experiments, the sample is mounted in the vacuum chamber to avoid the effect of THG from the ambient air. The light source is nanosecond OPO laser pumped with third-harmonic light of Nd:YAG laser (pulse width

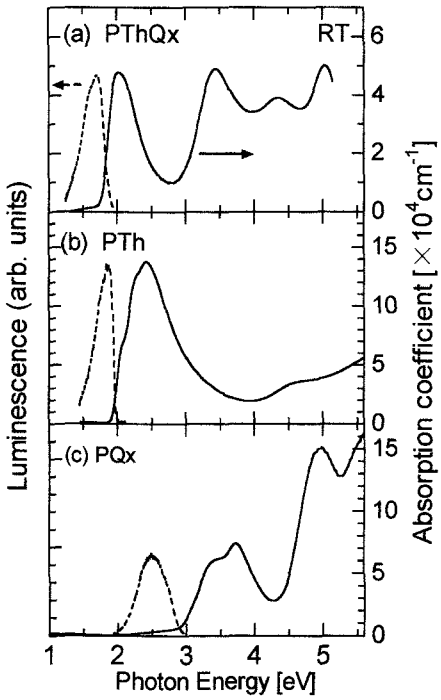

Fig. 2 Absorption (solid lines) and luminescence spectra (dotted lines) of PThQx (a), PTh (b), and PQx(c).

~6ns). The excitation light is focused onto the sample through lens. We determine $\chi^{(3)}$ values by comparing the intensity of THG from the sample with that from the reference (SiO_2). The latter is determined by the Maker fringe method.

3. RESULTS AND DISCUSSION

3.1 Absorption and luminescence

Figure 2 (a) shows the absorption and luminescence spectra of PThQx. PThQx shows three absorption peaks from visible to UV region. For comparison, the absorption and luminescence spectra of the homopolymers, head-to-tail poly(3-hexylthiophene) (PTh) and poly(heptyloxyquinoxaline) (PQx), are also presented in the Fig. 2 (b) and (c), respectively. The absorption and luminescence peak energies of PThQx are not located between those of PTh and PQx, but lower than them. In donor-acceptor type copolymer, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of

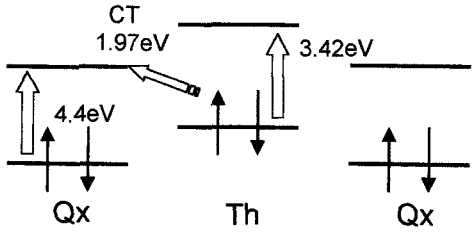

Fig. 3 Energy level structure in PThQx. Assignment of absorption spectra of PThQx is also shown.

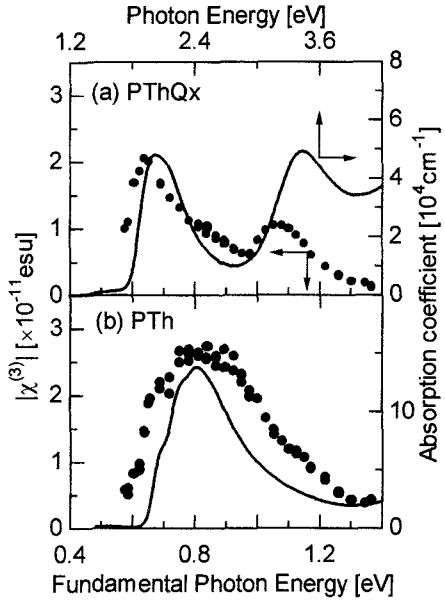

Fig. 4 THG spectra (dots) of PThQx (a) and PTh (b). The absorption spectra (solid lines) are also shown.

donors and acceptors are modulated depending on the respective ionization potentials. The HOMO of donors is relatively higher and the LUMO of acceptors is relatively lower as shown in Fig. 3. Resultantly, the lowest charge excitation is the CT from the HOMO of donors to the LUMO of acceptors. Thus, the optical gap is of CT type. The optical gap energy in the CT copolymers is smaller than those of homopolymers, PTh and PQx. The second (3.42eV) and third (4.4eV) absorption peak in PThQx can be assigned to the intramolecular excitations as shown in the Fig. 3.

As for the magnitude of the absorption coefficient (α), PThQx shows the smallest value among the three polymers. Generally, in one-dimensional semiconductors, the oscillator strength concentrates on the optical gap, which is due to the divergence of density of state characteristic in one-dimensional electronic systems or due to the one-dimensional exciton effect. In copolymer, however, both effects are relatively suppressed because of the CT character of the lowest excited state. As a result, the absorption coefficient related to the gap transition decreases and that related to the intramolecular absorption in the higher energy region rather increases.

3.2 Third-harmonic generation (THG)

The THG spectrum of PThQx is shown in Fig. 4(a). For comparison, the THG spectrum of PTh is also shown in Fig. 4(b). The maximum value of $\chi^{(3)}$ in PThQx is 2×10^{-11} esu, which is comparable to that of PTh. The $\chi^{(3)}$ spectrum of PThQx has two peaks around 0.65eV and 1.05eV. That is in contrast with the single-peak spectrum of PTh. In PThQx, the 0.65-eV peak is assigned to three-photon resonance to the CT state. As for the 1.05-eV peak, there are two possible origins. The first one is the three-photon resonance to the higher-

energy absorption peak that is assigned to the intramolecular absorption. The other one is the two-photon resonance to the one-photon forbidden state located around 2.48eV, which is observed in the two-photon absorption measurements [4]. These two origins are not exclusive. If the two coexists, they interfere with each other because the phases of $\chi^{(3)}$ around the two-photon resonance and the three-photon resonance in THG are generally different by π. For the estimate of the respective contribution of these two possible origins, the detailed spectral analysis is required.

Thus, PThQx shows the large $\chi^{(3)}$ values comparable to PTh. On the other hand, the absorption coefficient is smaller in PThQx. Let us consider this behavior based on the magnitude of the transition dipole moments contributing the third-order nonlinear optical processes. Dixit *et al.* proposed that the third-order optical nonlinearity in one-dimensional semiconductors can be described by the three *essential states* [5], which are the ground state |0>, one-photon allowed state |1> and one-photon forbidden state |2>. Moreover, perturbation theory gives us a simple expression of the nonlinear susceptibility of THG relevant to the essential states [6]:

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = \frac{N}{\varepsilon_0}\frac{e^4}{\hbar^3}\frac{<0|x|1><1|x|2><2|x|1><1|x|0>}{(\omega_1 - i\Gamma_1 - 3\omega)(\omega_2 - i\Gamma_2 - 2\omega)(\omega_1 - i\Gamma_1 - \omega)} \quad \cdots(1)$$

According to the eq. (1), the magnitude of $\chi^{(3)}$ is governed by the three factors. They are the transition dipole moment from the ground state |0> to one-photon allowed state |1>, <0|x|1>, the transition dipole moment between one-photon allowed state |1> and one-photon forbidden state |2>, <1|x|2>, and the energy denominators. <0|x|1> is related to the oscillator strength f : $f \propto <0|x|1>^2$. The absorption coefficient is proportional to the oscillator strength. Therefore, the small absorption coefficient in PThQx suggests the small <0|x|1>. Since $\chi^{(3)}$ is proportional to the square of <0|x|1><1|x|2>, the large $\chi^{(3)}$ with the small absorption coefficient in PThQx indicates the large <1|x|2>.

Next, let us consider the physical origin of the small <0|x|1> and the large <1|x|2> in PThQx in Fig. 5. The simplified schematic of the excited states of CT-type copolymer is compared with that of normal conjugated polymers. In CT copolymers, the in-phase and out-of-phase linear combination of the leftward and rightward CT transitions form the odd- and even-parity CT states, |1> and |2>. On the other hand, in normal conjugated polymers, the lowest excited state corresponds to the on-site charge excitation and the second lowest excited state is to the CT excited states. Generally the optical absorption is approximately proportional to the amplitude to the on-site excitation. Therefore, the linear absorption of CT copolymer will be small as compared with that of the homopolymers. As for the transition dipole moments between the odd and even excited states <1|x|2>, its magnitude reflects the similarity about the spatial extension. In CT copolymer, the spatial extensions of the two excited states |1> and |2> tend to be similar to each other. Consequently, <1|x|2> can be large in CT copolymer. In homopolymers, the spatial extensions of the wave functions of the two excited states |1> and |2> are quite different. Therefore, <1|x|2> can not be large in normal conjugated polymers.

The large $\chi^{(3)}$ with small absorption coefficient in PThQx leads to the enhancement of the figure of merit, which is defined as $\chi^{(3)}/\alpha$. In nonlinear optical devices, the absorption gives rise to real charge excitation, which induces the energy loss and the reduction of the repetition rate of nonlinear optical response. Therefore, the small absorption coefficient is desirable in nonlinear optical materials. In PThQx, the large $\chi^{(3)}$ is realized though the absorption is reduced. Therefore, the large figure of merit is obtained. Thus, the CT-type copolymer is a good nonlinear optical material.

4. SUMMARY

We have performed the THG measurements on the CT-type conjugated copolymer, PThQx. Its $\chi^{(3)}$ value is comparable to that of a typical conjugated homopolymer, PTh, though the absorption coefficient is smaller in PThQx. In PThQx, CT nature of the excited state reduces the transition dipole moment from the ground state to the odd excited states, but enhances the transition dipole moment between the odd and even excited states. Consequently, PThQx shows the large $\chi^{(3)}$ and the small α which lead to large figure of merit for nonlinear optical response. From these results, we can conclude that the CT type copolymer is a promising nonlinear optical material.

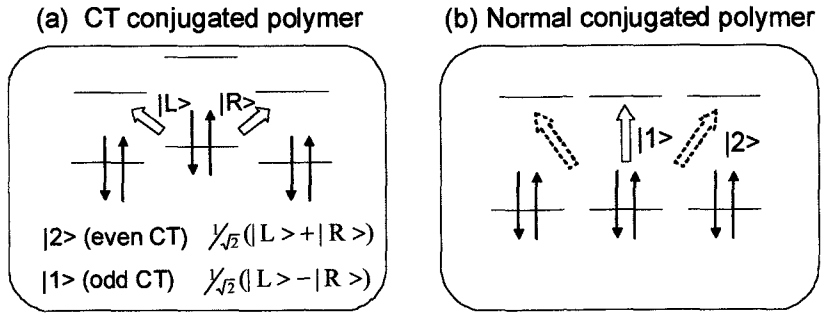

Fig. 5 Schematics of excited states in CT conjugated polymers (a) and normal conjugated polymers (b).

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