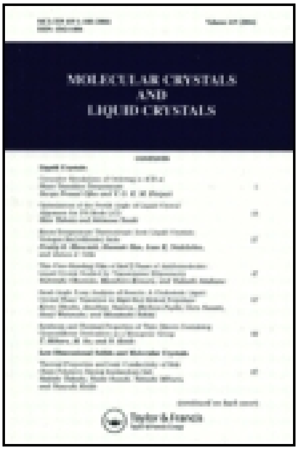

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Nonlinear Electronic Phenomena in Low Dimensional Organic Solids

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NONLINEAR ELECTRONIC PHENOMENA IN LOW DIMENSIONAL ORGANIC SOLIDS

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Abstract Unique nonlinear phenomena observed in electrical and optical properties of quasi one-dimensional organic solids are reviewed. Possible relevance of these phenomena to the molecular electronics and optoelectronics is discussed.

INTRODUCTION

The state-of-art technology of inorganic semiconductors is developing toward the direction of diminishing dimensions of device structures to utilize the quantum confinement effect. However, as the size of the microstructures is reduced to a subnanometer scale, technical problems in the device fabrication become increasingly serious[1] .

In the meantime, the concept of molecular devices has sprouted out with a hope of utilizing "natural quantum confinement effect" in organic molecules and molecular aggregates. The central problems in this quest are; (1) design and synthesis of new functional organic molecular assemblies, and (2) exploration of novel concepts of functions which are hardly realized in the conventional inorganic materials.

In this paper, we review some recent results of our group in quest of future possibilities of molecular optoelectronics in the direction mentioned above. An emphases is placed on the nonlinear phenomena found in the electrical and optical properties of some groups of quasi one-dimensional (1D) organic substances.

ELECTRICAL NONLINEARITY IN QUASI-1D ORGANIC COMPLEX CRYSTALS

Among a large number of organic charge-transfer (CT) complex crystals composed of quasi-1D stacks of donor and acceptor molecules, so-called mixed-stack complex crystals usually show semiconductive properties, in contrast to segregated-stack CT crystals, such as TTF-TCNQ, showing metallic properties. When these mixed-stack complex crystals are located near the so-called neutral-ionic (NI) phase boundary,[2] the ground state of crystal consists of an appreciable mixture of both the neutral and ionic molecular states. In this sense, these organic molecular compound semiconductors are an analog of inorganic binary compound semiconductors, such as GaAs or ZnSe, having a mixed ionic and covalent character.

However, in the case of mixed-stack organic crystals, the electronic properties are essentially determined by the dynamics of solitons and domain-walls, in contrast to the one-electron band-structure regime established for inorganic semiconductors. A consistent interpretation of optical, electrical and magnetic properties of a number of mixed-stack organic crystals has been attempted. [3,4]

One of most spectacular features of the soliton dynamics is the remarkable nonlinear electric conductivity which is more remarkable in the quasi-ionic crystals. Characteristic negative resistance effect is often observed, when the electric field exceeds a certain threshold value E_{th}.[5-7] An example of such an electrical nonlinearity is shown in Fig. 1 for $TTeC_1TTF$-TCNQ, a mixed-stack crystal composed of $TTeC_1TTF$ as doner and TCNQ as acceptor.[7] Quite similar electrical nonlinearities were also observed in many other mixed-stack crystals and in some alkaline-metal-TCNQ complex crystals such as K-TCNQ and Rb-TCNQ.[8] In latter crystals, the dimerized 1D stacks of fully ionized TCNQ molecules are in a BOW state which can support the charged soliton excitations. The experimental values for the threshold field E_{th} range from 10 to 1 kV/cm, which are considerably lower than the threshold for a dielectric breakdown process.

At the early stage of molecular electronics, there was an idea that the nonlinear soliton dynamics in some organic systems might be utilized, for instance, as a soliton switch.[9] At that time, however, there was little chance of examining the reality of this idea. The result shown below provides the first experimental demonstration of "a nonlinear soliton device", where characteristic nonlinear conductivity discovered in organic CT crystals is playing an essential role.

This "molecular device" is composed of a small piece of $TTeC_1TTF$-TCNQ single crystal connected to a dc voltage supply V_0 and a load resister R_L (=33kΩ) in series, as shown in the inset of Fig. 1. The crystal is cooled to a temperature below 180 K, where a sharp switching behavior can be observed. The relation between the ac current I and the ac voltage V is seen on a CRT display as a Lissajou's curve (Fig.2). When the amplitude of V is small, the circuit current is limited by the high ohmic resistance of crystal (>>R_L). But, when the amplitude of ac voltage is increased to a certain threshold, the circuit current is switched on to a negative resistance state (cf. Fig. 1), where the circuit current is practically limited by the load resistor R_L. This "on" state can be switched off, when the voltage is lowered below a lower threshold. There is a remarkable hysteresis in this on-off cycle, as seen in Figs.1,2, indicating a cooperative nature of the negative resistance effect.

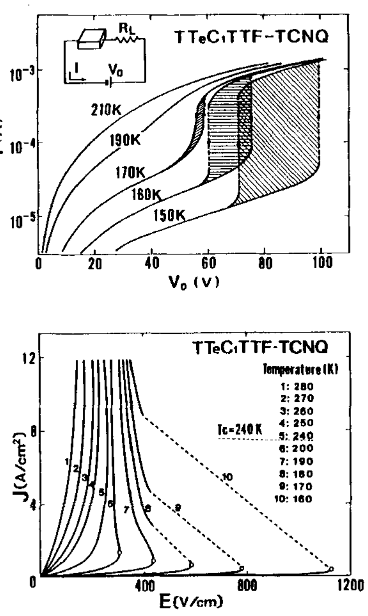

FIGURE 1 Nonlinear electric properties of $TTeC_1TTF$-TCNQ crystal (from ref. [7]).

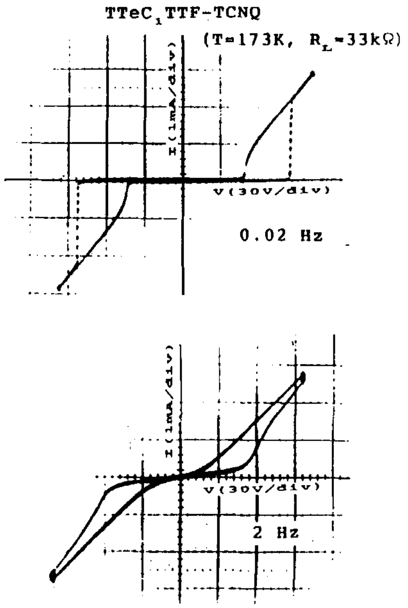

FIGURE 2 Current-voltage characteristics of an electric bistable device using $TTeC_1TTF$-TCNQ cryatal at 173 K (R_L=33KΩ).

The operation of this "molecular device" is quite durable for repeated on-off cycles, but the response is very slow (at most of 10 ms [7]) and must be operated at low temperatures. Higher working temperature can be achieved by using CT crystals with higher critical temperature T_C of the BOW state. In fact, in Rb-TCNQ (T_C=381K), the current-switching effect is observable up to about 250 K.[8] To shorten the response time, we shall have to reduce the size of crystal, since the negative resistance effect is a cooperative phenomenon occurring within the bulk of crystal. It is interesting to note that polycrystalline films of some CT complexes, such as Ag,Cu-TCNQ, have been reported to exhibit a similar current-switching effect at room temperature with a very fast response time (a few ns).[10] It is challenging to examine if there is any correlation between the mechanisms of these unconventional nonlinear effects observed in both crystals and films of organic CT complexes. Optical trigger of the switching, as observed in Cu-TCNQ films,[10] may be feasible in the crystal device by utilizing recently discovered photoinduced valence instability effect.[11]

OPTICAL NONLINEARITY IN QUASI 1D ORGANIC SEMICONDUCTORS

Semiconducting properties of conjugated polymers are interpreted in terms of charged solitons or polarons, which are relaxed states of carriers (electrons or holes) coupled to the 1D structure of polymer backbone chains. By contrast, the remarkable nonlinear optical (NLO) properties of these polymers are predominantly determined by the unrelaxed states of photo-generated electron-hole pairs (excitons) in the 1D backbone chain. The concept of 1D exciton is rather classical,[12] but it is under current interest in the study of a quantum wire structure of conventional semiconductors. The same concept may be also applied as well to the quasi 1D electronic systems in conjugated polymers.

We shall mainly deal with centrosymmetric systems where the lowest-order NLO response is represented by a third-order (cubic) optical susceptibility $\chi^{(3)}$. The large and very fast third-order response of conjugated polymers is promising for photo-refractive materials which play a key role in the all-optical NLO devices.

To demonstrate characteristic NLO features of 1D excitons in conjugated polymers, we show in Fig. 3 recent experimental results for a π-conjugated polymer polydiacetylene (PDA) and for a σ-conjugated polymer polysilane (PS). In this figure, the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ spectra are plotted against the photon energy of fundamental laser light, while the absorption spectra (solid lines) against the three-photon energy, at which the third-harmonic light is observed. At a glance, we can notice that the $\chi^{(3)}$ spectra show rich features, indicating the contributions of various multi-photon resonance channels in the NLO process.

The NLO data shown in Fig. 3 have been obtained by the third-harmonic generation (THG) measurements on PDAs[13,14] and PSs.[15,16] Another useful means of NLO study is the electro-modulation spectroscopy (electro-absorption or electro-reflection), in which we apply an ac electric field to a sample and measure modulated intensities of transmitted or reflected light at the second harmonic frequency (the Kerr effect) as a function of photon energy. The electro-modulation spectroscopy on organic crystals has been pioneered by Sebstian et al. in detecting the charge transfer transitions in aromatic crystals.[17] The same technique is now recognized as a powerful means of NLO spectroscopy of organic NLO materials.[18] The usefulness of this method in the NLO spectroscopy comes from the capability of detecting optically forbidden states which are not active in the linear response but are playing a substantial part in various channels of the NLO process.[14,19]

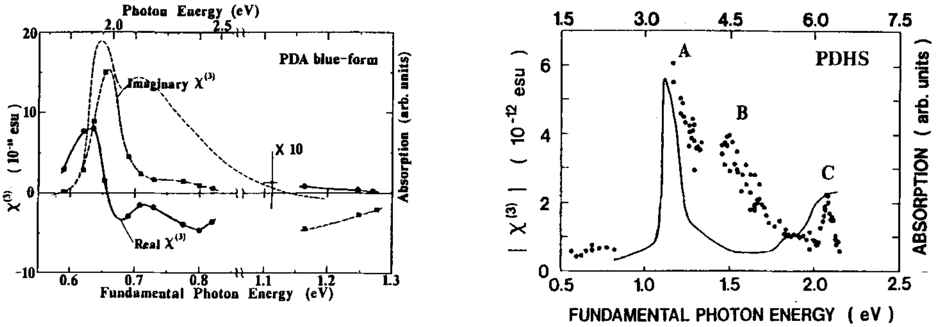

FIGURE 3 Third-order optical nonlinearities in π-conjugated polymer polydiacetylene (left) and σ-conjugated polymer polysilane (right). Solid lines represent ordinary absorption spectra.

Systematic measurements of THG, electro-modulation, and sometimes two-photon absorption spectra of PDAs,[14] PSs,[15,16,19] and also of other quasi-1D dimensional organic substances, such as platinum(M)-halogen(X) chain complexes[20], have been made aiming at experimental and theoretical elucidation of underlying electronic mechanism. As a result, it turned out that the NLO properties of these organic materials can be analyzed at a quantitative level in terms of a concept of 1D excitons which are more or less delocalized over several constituent molecular units. In this sense, the future development of organic NLO materials is significantly dependent on an extent how we can control and optimize the properties of 1D excitons to meet various technological requirements. Efforts toward this goal have started just recently.

SUMMARY

In the exploration of "unconventional substances" for "unconventional optical applications", some organic semiconductors offer new possibilities which are hardly achieved by conventional inorganic semiconductors. Examples were demonstrated for remarkable nonlinear current-voltage characteristics discovered in some organic CT crystals and for nonlinear optical properties of conjugated polymers. In both types of nonlinearities, quasi-one-dimensionality in their electronic structures is essential, giving rise to the nonlinear soliton excitations in the former type and to the 1D excitons in the latter type materials. The present stage of study remains at a rather premature level as yet, but we may anticipate that new fields of molecule-based technology will be established in future on an interdisciplinary ground connecting condensed matter physics, organic chemistry, polymer chemistry, and photo-electronics.

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