

Thiophene-Based Semiconducting Materials: Integrated Functionalities of Electronics and Photonics

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The structure and property characteristics of thiophene-based molecular semiconductors are outlined. The importance of the molecular alignments in thin films and crystals will be stressed.

Key words: polythiophene, oligothiophenes, thiophene/phenylenes co-oligomers, molecular alignment, FET, SNE

1. INTRODUCTION

The research and development of thiophene-based semiconducting materials have long history. Polythiophene, one of the best-known materials among them, was first synthesized by Yamamoto et al. [1] as a well-defined form. This was followed by the development of various analogues, including a variety of soluble and processible polythiophene derivatives [2]. Meanwhile, oligothiophenes, which were originally found as naturally-occurring compounds [3], were synthesized and developed [4]. An advantage for this is that the chain-length (or molecular-weight) dependent physical properties can systematically be investigated. Garnier and co-workers [5] studied the charge transport features of the oligothiophenes on electronic device configurations such as field-effect transistors (FETs).

More recently, hybridized materials are being added to this important class of thiophene-based molecular semiconductors. Examples include those hybridized with fluorenes [6] and phenylenes [7] at molecular level. Hotta and co-workers [8] have systematically developed thiophene/phenylene co-oligomers as a typical example. One of the advantages of this novel class of molecular semiconductors is that extension of the π -conjugation can be tuned as desired by changing the total ring number of the thiophenes and phenylenes and their mutual arrangement in the molecule. Moreover, the molecular shapes can be varied as well, producing e.g. bent and zigzag molecules.

In the present studies the author presents various thiophene-based molecular semiconductors (see Fig. 1) and their unique features of the structure and electronic and optical properties in the form of thin films and crystals with emphasis upon the oligomer materials, especially thiophene/phenylene co-oligomers. In these materials functionalities of electronics and photonics are nicely integrated.

2. THIOPHENE-BASED MATERIALS

2.1 Polythiophenes

One can make the polythiophene soluble by putting long alkyl chains (e.g. hexyl groups) at 3-position [2] of the thiophene ring [refer to Fig. 1(a)]. The resulting polythiophene derivatives possess good mechanical drawability and the polymer backbones tend to align in the drawn direction. This immediately enables one to

extensively investigate structure/property relationship. As an example Hotta et al. [9] measured IR spectra polarized either parallel or perpendicular to the drawn direction. Figure 2 shows the spectra for poly(3-hexylthiophene) films partially oxidized with iodine after being drawn by 5 times initial length. The doping-induced modes (marked with asterisks in Fig. 2) are clearly intensified along the drawn direction. A broadband around 4000 cm^{-1} due to subgap transition is again highly polarized along the drawn direction. (Note that the ring-stretching mode at 1510 cm^{-1} and the CH out-of-plane deformation mode at 825 cm^{-1} are intensified in reverse with respect to the polarized measurements.) These observations obviously demonstrate that one-dimensional electronic processes dominate along the aligned polythiophene backbones.

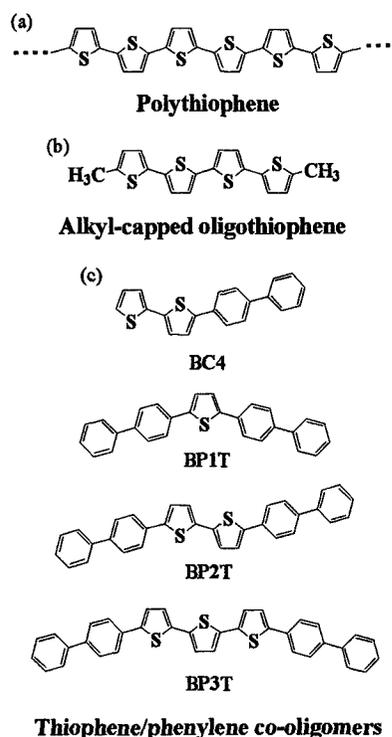


Fig. 1 Various thiophene-based molecular semiconductors.

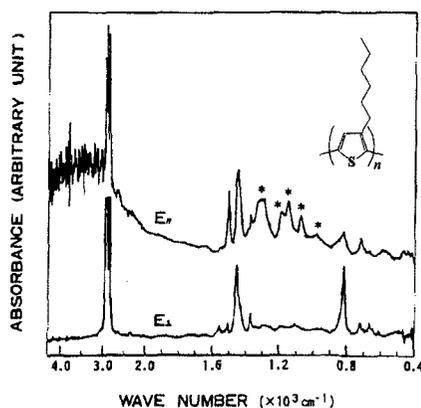


Fig. 2 Polarized IR absorption spectra of drawn poly(3-hexylthiophene) films partially doped with iodine. E_{\parallel} and E_{\perp} denote the electric fields polarized parallel and perpendicular to the drawn direction, respectively. Asterisks indicate the doping-induced modes. Reprinted with permission from Ref. 9. Copyright 1989 American Chemical Society.

2.2 Oligothiophenes

Molecules [i.e. molecular long axis, as defined as a line connecting the two terminal methyl carbons in Fig. 1(b)] take vertical disposition against the substrate plane (in the case of the thin films) or crystal faces of the flake crystals because of strong π - π interaction among molecules. Unlike the polythiophene, charge transport takes place perpendicular to the molecular long axis through the face-to-face molecular assembly [10]. The alkyl-caps for the oligothiophenes produce both structural regularity and enhanced carrier mobility [10,11]. Making use of these characteristics, Akimichi et al. [12] made electrical measurements with FETs having on the channel thin films of a series of the alkyl-capped oligothiophenes with different lengths (Fig. 3).

Waragai et al. [13] further pursued their temperature-dependent electrical measurements and concluded that the charge transport is governed by thermal hopping of molecular polarons.

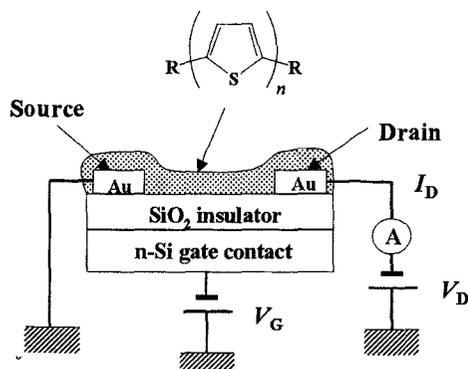


Fig. 3 Schematic diagram of an FET device. Reprinted with permission from Ref. 12. Copyright 1991 American Institute of Physics.

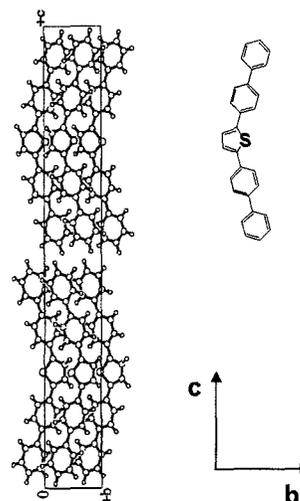


Fig. 4 Crystal structure of BPIT viewed along a -axis. Adapted with permission from Ref. 14. Copyright 2002 Wiley-VCH.

2.3 Thiophene/phenylenes co-oligomers

Varied molecular shapes of the title co-oligomers provide them with peculiar crystallographic features. Hotta and Goto [14] pointed out how the molecular long axis of BPIT [defined as a line connecting the two terminal p -phenyl carbons in Fig. 1(c)] is disposed perpendicular to the ab -plane (see Fig. 4). The angle between the molecular long axis and the normal of the ab -plane is only 1.0° , in striking contrast to the conventional oligothiophenes and oligophenylenes to which the corresponding angle is $\sim 20^\circ$ [15]. This feature leads to various interesting aspects as outlined below.

3. STRUCTURE AND MOLECULAR ALIGNMENT

3.1 Self-assembled upright alignment

In free-grown flake-shaped crystals (or thin films deposited on a non-oriented substrate), the oligomer molecules tend to be self-assembled so that the molecules form a layered structure in which the molecular long axis can be aligned nearly vertical against the crystal faces (or substrate plane) as schematically represented in Fig. 5(a) and (b), left. Suppose the crystals and thin films comprise many small domains. If the said axis is upright, the molecular long axes of the individual domains should be aligned along one direction [Fig. 5(a), upper right]. This is practically the case with BPIT (Fig. 4). For straight molecules such as oligothiophenes and oligophenylenes, however, this is no longer true [Fig. 5(b), right].

What follows is that rigorous molecular alignment is more readily achieved with the non-straight molecules like BPIT than for the straight molecules. As an example the author displays XRD diagrams (Fig. 6) and the corresponding incident-angle-dependent polarized absorption spectra (Fig. 7) for thin films of BC4 and BPIT. In Fig. 7 a sharpened line shows up and steeply grows around 300 nm with increasing incident angles [16], reflecting the virtually upright disposition of the molecules in the thin films.

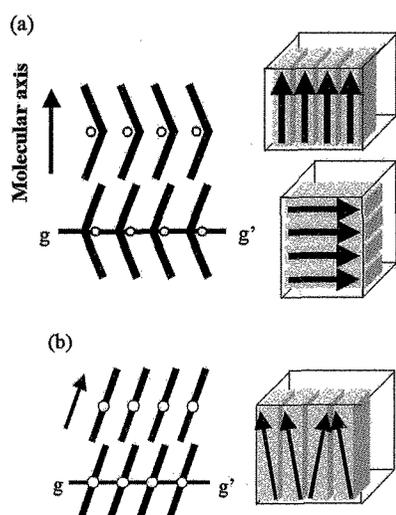


Fig. 5 Schematic representation of molecular alignments. (a) Upright and uniaxial alignments in non-straight molecular crystals. (b) For straight molecular crystals. Circles indicate the center of gravity for the molecules.

The aforementioned crystallographic feature is not restricted to BP1T. Hotta et al. [17] clearly show that this is more generally the case with molecular crystals comprising non-straight molecules e.g. BP2T, whose molecular shape is zigzag (see Fig. 1). If one closely looks at the crystal structure of BP1T, one immediately notices that with the biphenyl moieties in BP1T the lines connecting the 4,4'-carbons are oblique to the *c*-axis (at an angle $\sim 17^\circ$) [14]. In the crystal, therefore, the oblique disposition of the two biphenyls cancels out each other and, as a result, the molecular long axes stand nearly upright (Fig. 4).

3.2 Uniaxial alignment by epitaxy

If a strong interaction is present between the molecules and substrate, those molecules tend to lie with their long axes paralleling the substrate plane. In this case, one expects epitaxial growth of thin films and crystals in which the molecular alignment can be controlled in a manner different from that mentioned above. This is schematically depicted in Fig. 5(a), lower right. If a specific axis on the substrate plane is present and all the molecular axes are aligned along that direction, the uniaxial alignment will be achieved. This situation can be understood as follows: Imagine a plane defined by the upright axis [in Fig. 5(a), upper right] and the specific axis on the substrate. When one rotates the upright axis by an angle of 90° in the plane defined just above, this produces the uniaxial alignment.

Thus, both the upright and uniaxial alignments can analogously be dealt with. The point is that if the rigorous molecular alignment is attained in the upright disposition, such alignment can again be attained with the uniaxial disposition. In this sense the non-straight molecules typified by the thiophene/phenylenes co-oligomers are once again advantageous.

In fact, Yoshida et al. [18] achieved highly polarized emissions from thin films of BP n T ($n = 1-3$) deposited epitaxially on the ultra-thin films of poly(*p*-phenylene)

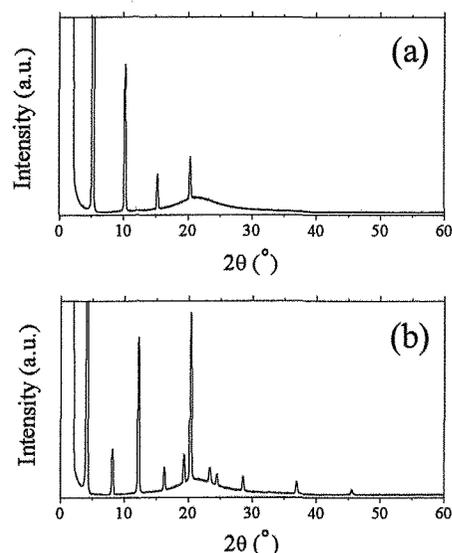


Fig. 6 XRD diagrams of the films of (a) BC4 and (b) BP1T. Reprinted with permission from Ref. 16. Copyright 2000 American Chemical Society.

(PPP) uniaxially aligned by friction. The direction of the aligned PPP chains determines the specific axis mentioned above. The polarized emissions result from the molecules aligned uniaxially along this axis. The emissions color-tuned blue to orange are clearly visible, red-shifted with the increasing number of the thiophene rings on the molecular core (see Fig. 1). The highest polarization ratio was 94 for the BP2T film (Fig. 8).

Another example of the uniaxial alignment includes the epitaxial growth of molecules on top of a cleaved surface of the (001)-plane for a KCL single crystal.

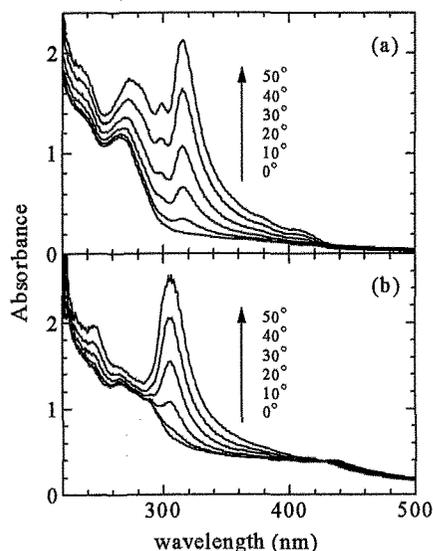


Fig. 7 Incident-angle-dependent polarized absorption spectra of films in 200-nm thickness for (a) BC4 and (b) BP1T. Reprinted with permission from Ref. 16. Copyright 2000 American Chemical Society.

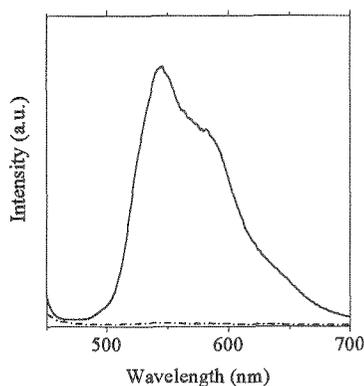


Fig. 8 Polarized emission spectra of BP2T. The polarization ratio was 93.5 at the emission maximum (546 nm). The spectra are polarized parallel (—) or perpendicular (---) to the friction direction of PPP. Reprinted with permission from Ref. 18. Copyright 2000 Wiley-VCH.

This method has originally been developed by Yanagi [19]. The essential point is that the ionic lattice distance of KCl along its [110] direction, 0.44 nm, plays a role for the epitaxial nucleation of the crystals. This is because the repeating interval of the phenyl and thiophene units is ~ 0.43 nm, being commensurate with the above inter-ionic size. Thus needle-shaped crystallites are formed along the two equivalent directions of [110] that cross each other at a right angle. Moreover, Yanagi et al. [19] mentioned that non-straight molecules can migrate on the surface until being incorporated to growing sites of the crystallites, because too strong interaction between the molecules and KCl anticipated for straight molecules is suitably mitigated for the non-straight molecules.

On the basis of this method, Ichikawa et al. [20] fabricated FET devices (Fig. 9) and estimated their action characteristics. They found the carrier mobility quite high (~ 0.7 cm²/Vs). This is partly because the needle axes of the crystallites penetrate the face-to-face molecular array through which the charge transport predominantly takes place. Notice that the needle axes and molecular long axes meet at right angles.

4. PHOTONIC FEATURES OF CRYSTALS

One of the most interesting features for the molecular semiconductors lies in their emission properties. This is especially the case with the crystals where transition dipole moments are disposed regularly. In particular, when the transition dipoles are upright against the crystal faces (Fig. 10), a large optical gain is expected, producing peculiar emission characteristics.

4.1 Spectrally-narrowed emission (SNE)

Whether semiconductors cause the laser oscillation is a pivotal issue on applying them to electro-optic devices. To examine this it is useful to photopump the material and see if the SNE occurs. Using crystals of thiophene/phenylene co-oligomers, Nagawa et al. [21] and Ichikawa et al. [22] studied their emission properties

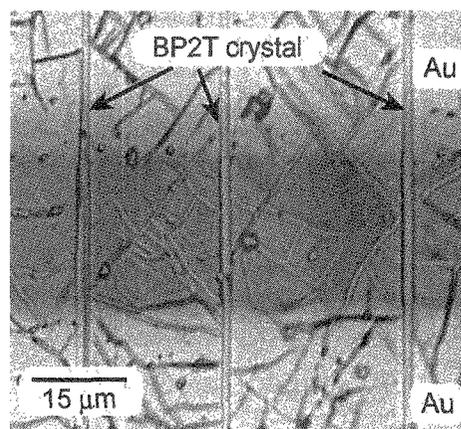


Fig. 9 Optical microscope image of the FET device. Reprinted with permission from Ref. 20. Copyright 2002 Wiley-VCH.

and found out that several kinds of co-oligomers definitively cause the SNE (FWHM: a few nanometers). They attributed this to amplified spontaneous emission (ASE). As an example, Fig. 11 shows the ASE from BP1T crystals [21], as compared with broadband photoluminescence (PL) taken with photoexcitation of lower intensity. The ASE has also been noted for melt-recrystallized materials of this class of co-oligomers [23]. Shimizu et al. [24] observed much narrower emission lines from a BP1T crystal by photopumping a long slender region within the crystal.

Recently, the SNE was observed for various kinds of semiconductors such as spin-coated conducting polymers [25] and dye-dispersed polymers [26]. Nonetheless, the SNEs from crystals yet remain scarce [27,28]. In this context the thiophene/phenylene co-oligomers can be counted among one of the best candidates with photonic high functionalities. Once good photonic characteristics represented by the SNEs are combined with the charge transport properties of a high level exemplified by the FET devices, further advanced high functionalities are expected to be accomplished.

4.2 Other related phenomena

In relation to large oscillator strengths of the oligomer molecules, further interesting optical properties follow. Examples include the Davydov splitting of excited states in crystals.

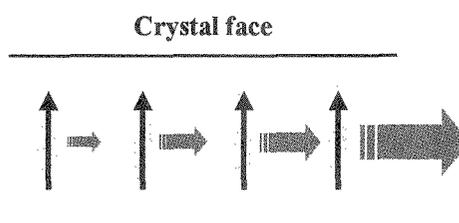


Fig. 10 Large optical gain along the crystal faces produced by the upright molecular alignment.

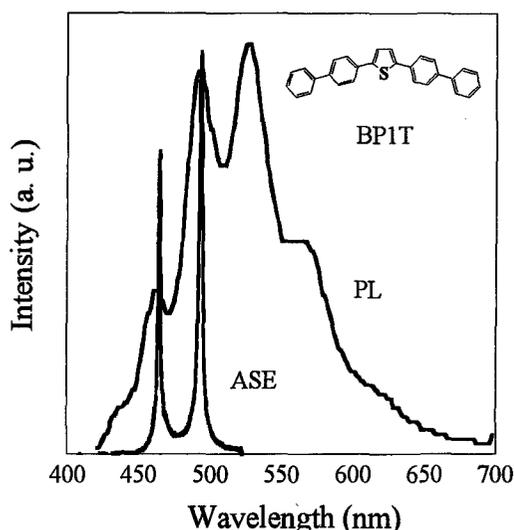


Fig. 11 ASE from BP1T crystals, as compared with PL.

Figure 12 represents an energy diagram that can typically be seen for molecular crystals including four molecules in a unit cell. Since in e.g. the crystals of BP1T all the symmetry operations except the unit element commute the lattice points on which the molecules reside, the site group is C_1 [29,30]. Therefore, the representation of the excited state is reduced to $A_g + B_g + A_u + B_u$ and, hence, its energy level is to split into four [29,30]. Of these symmetric species, only A_u and B_u are associated with the optical transition [31] and the energy separation between these two states determines the Davydov splitting. Because of the large oscillator strength of the molecules, this splitting is large; for BP1T Hotta et al. estimated the magnitude of the Davydov splitting to be 19000 cm^{-1} [16].

The magnitude of the Davydov splitting also represents that of the exciton band width [32]. This band width may well be sufficiently large so that the excitons can be stabilized at room temperature. This is one of great advantages of using molecular semiconductors. If this is the case, one expects that the excitons will strongly interact with a photon field in the crystals. This interaction results most likely in generation of polaritons [33]. An expected dispersion relation is given in Fig. 13. In this diagram A_u excitons interact photons with the same symmetry (i.e. polarized along the b -axis), generating polaritons that also belong to the same symmetry.

Polarizability tensors always involve totally symmetric species regardless of the point groups of crystals. In the specific case represented in Fig. 13, therefore, the direct product among the polarizability tensor and upper and lower polariton branches should include a totally symmetric species. This implies that the polariton-mediated transitions are Raman active [34]. Indeed Yanagi et al. [35] observed the stimulated Raman scattering (on a resonant condition) which is not due to the molecular origin, but reflects the coherence encompassing the whole crystals. This is consistent with the above statement.

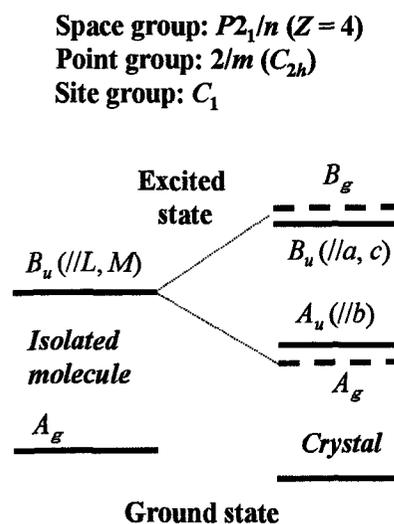


Fig. 12 Electronic states in crystals.

5. CONCLUSION AND FUTURE OUTLOOK

The author outlined the structural features and physical properties of the thiophene-based molecular semiconductors. In the polythiophene and its derivatives one-dimensional electronic processes dominate along the aligned polythiophene backbones. The oligomer materials of oligothiophenes and thiophene/phenylene co-oligomers exhibit a well-defined structure where the molecules take the vertical disposition. In crystals and thin films of the latter oligomers, in particular, the molecular alignment can be controlled more rigorously. This leads to many interesting aspects in both electronic and photonic processes.

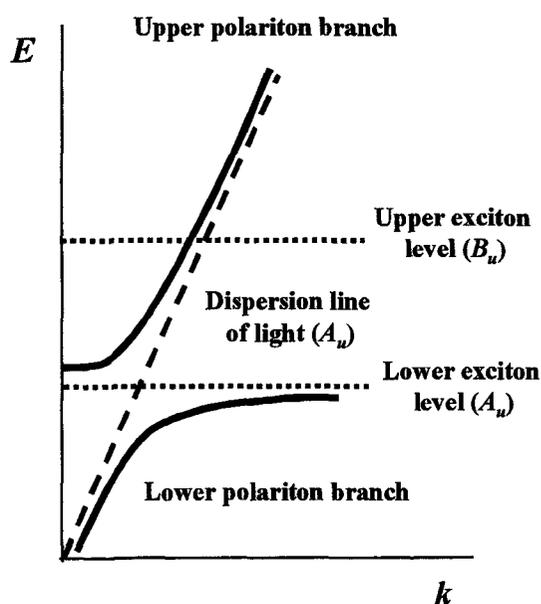


Fig. 13 Dispersion relation for light and exciton in matter.

The author highlighted highly polarized absorption in thin films of thiophene/phenylene co-oligomers where the self-assembled molecules take the upright disposition against the substrate plane. The uniaxial alignment results from the epitaxial growth of the oligomer molecules. In this case, again, the thiophene/phenylene co-oligomers exhibit the highly polarized emissions. Another elegant example of their uniaxial alignment is achieved on single crystals of KCl as the substrate. The resulting needle-shaped crystallites show high carrier mobility on the FET device configurations. Moreover, the crystals produce various advanced photonic features. The SNEs and stimulated resonance Raman scattering are typical examples.

These integrated electronic and photonic characteristics will open up a path toward further advanced device applications in the near future.

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