

from polymer **III** to **I** correlates with an increase in the photorefractive grating buildup time from polymer **I** to **III**. High photoconductivity and quantum yield means a fast rate to build up a static space-charge field necessary for the PR effect. The diffraction efficiency,  $\eta$ , defined as the ratio of the diffracted to incident reading beam power, was also recorded in DFWM experiments. Because the diffraction efficiency is determined by the amplitude of the index grating, a behavior similar to the optical gain is expected if the PR effect is mainly responsible for the formation of the index grating. As illustrated in Figure 5, the diffraction efficiency increases super-linearly with increasing applied field and exhibits a similar trend to the gain coefficient. At  $E = 60 \text{ V}/\mu\text{m}$ , the achieved diffraction efficiencies for polymer **II** and **III** were 13.0 and 17.8 %, respectively.

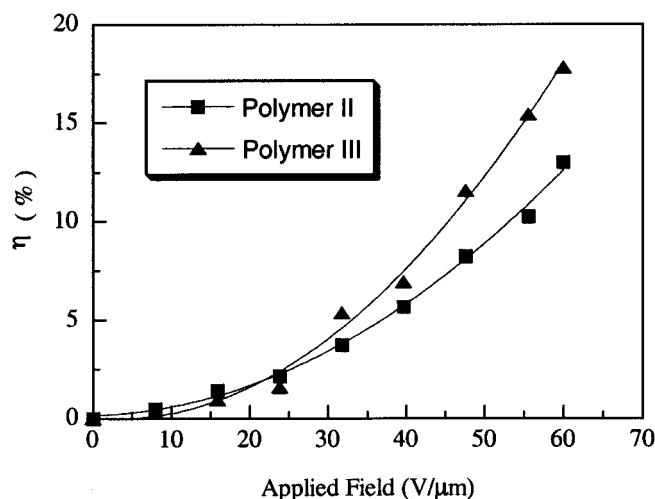


Fig. 5. Variation of the diffraction efficiency with the applied field of polymers **II** and **III**.

In summary, we have developed novel fully functionalized photorefractive polymers that take advantage of the unique photophysical properties of transition metal phthalocyanine and porphyrin complexes. The high PR performance of polymers containing Zn phthalocyanine and porphyrin complexes is the result of large photoconductivity and photogeneration quantum yield. The unpaired spin is found to be detrimental to PR performance because it provides an efficient channel for the relaxation of the excited state and thus reduces the quantum yield of photogeneration of charge carrier.

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[10] Elemental analysis results: Polymer **I**: Anal. Calcd. for  $C_{66.54}H_{95.68}N_{1.04}O_{2.51}Cu_{0.01}$ : C, 82.04; H, 9.82; N, 1.49; Cu, 0.065. Found: C, 81.41; H, 9.51; N, 1.44; Cu, 0.072. Polymer **II**: Anal. Calcd. for  $C_{66.54}H_{95.68}N_{1.04}O_{2.51}Zn_{0.01}$ : C, 82.04; H, 9.82; N, 1.49; Zn, 0.067. Found: C, 81.27; H, 9.57; N, 1.52; Zn, 0.071. Polymer **III**: Anal. Calcd. for  $C_{66.3}H_{95.31}N_{1.07}O_{2.02}S_{0.99}Zn_{0.01}$ : C, 81.98; H, 9.81; N, 1.54; Zn, 0.067. Found: C, 81.04; H, 9.37; N, 1.49; Zn, 0.070. Polymer **IV**: Anal. Calcd. for  $C_{66}H_{95}N_{1}O_{2}S_1$ : C, 82.08; H, 9.84; N, 1.45. Found: C, 81.90; H, 9.92; N, 1.31.  
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### Charge Transport versus Optical Properties in Semiconducting Crystalline Organic Thin Films\*\*

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Thin films of  $\pi$ -conjugated materials are currently widely tested for exploitation in devices such as light-emitting diodes (LEDs)<sup>[1,2]</sup> or field-effect transistors (FETs).<sup>[3-5]</sup> The body of

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knowledge accumulated over the years has triggered improvements in performance to the point where these organic-based devices start competing with their inorganic counterparts. However, there is still a fundamental need to understand at the microscopic level the relationships between the solid-state packing of chains and the resulting charge transport and optical properties; establishing such relationships would open the development of new strategies towards enhanced bulk mobility of charge carriers in FETs and high electroluminescence quantum yield in LEDs.

To gain this understanding requires an adequate characterization of the interchain interactions. The key role of these (non-covalent) interactions has been demonstrated in numerous instances; for example, the mobility of charge carriers in  $\alpha$ -sexithienyl thin films is measured to be highly sensitive to the degree of local ordering of the chains<sup>[4,6]</sup> and it is found that going from solutions to thin films provokes a dramatic decrease in photoluminescence quantum yield.<sup>[7]</sup> From a theoretical standpoint, the phenomenological models used to describe transport properties<sup>[8–11]</sup> and the molecular excitonic theories addressing the optical properties of interacting units,<sup>[9,12]</sup> have been able to provide mostly a qualitative picture. Here we illustrate how correlated quantum-chemical treatments of the interchain effects allow quantitative estimates of the parameters governing both the transport and optical properties. This is exemplified via a detailed comparison of the properties of  $\alpha$ -sexithienyl (6T)<sup>[13]</sup> and  $\alpha$ - $\alpha'$ -bisdithieno[3,2-b:2',3'-d]thiophene (BDT)<sup>[14]</sup> crystals. The choice of these two compounds is motivated by their promising use in organic FETs<sup>[3–5,15]</sup> and their very different crystal packing, as shown in Figure 1 (where the relative locations of the molecules within the *bc* layer are displayed). When compared to 6T, the BDT crystal is characterized by a more efficient molecular orbital overlap of units aligned along the *b* axis, which is expected to impact strongly on the transport and optical properties.

Our theoretical approach consists of tracking the structure–property relationships from the results of correlated quantum-chemical calculations performed on *supermolecular structures*, extracted from the single-crystal structures of BDT<sup>[14]</sup> and 6T at low temperature.<sup>[13]</sup> We make use of the semiempirical intermediate neglect of differential overlap

(INDO) Hamiltonian, developed by Ridley and Zerner,<sup>[16]</sup> to calculate the electronic structure of the clusters and extract quantitative estimates of the interchain transfer integrals. The INDO method is then coupled to a single configuration interaction (SCI) scheme in order to investigate at the correlated level the impact of interchain interactions on the absorption and luminescence properties;<sup>[17]</sup> the reliability of this approach is justified by the fact that the INDO Hamiltonian has been parameterized by Zerner and co-workers in order to reproduce the optical absorption spectra of organic molecules when coupled to an SCI scheme. Except when stated otherwise, the CI calculations mix all the possible intrachain and charge-transfer one-electron excitations between the  $\pi$ -levels; this is a major improvement compared to traditional excitonic theories in which the charge-transfer contributions are neglected;<sup>[9,12]</sup> it allows distinction between intrachain (Frenkel-like) and interchain excitations.

First, we analyze the dispersion of the valence/conduction bands built via interaction of the HOMO (highest occupied

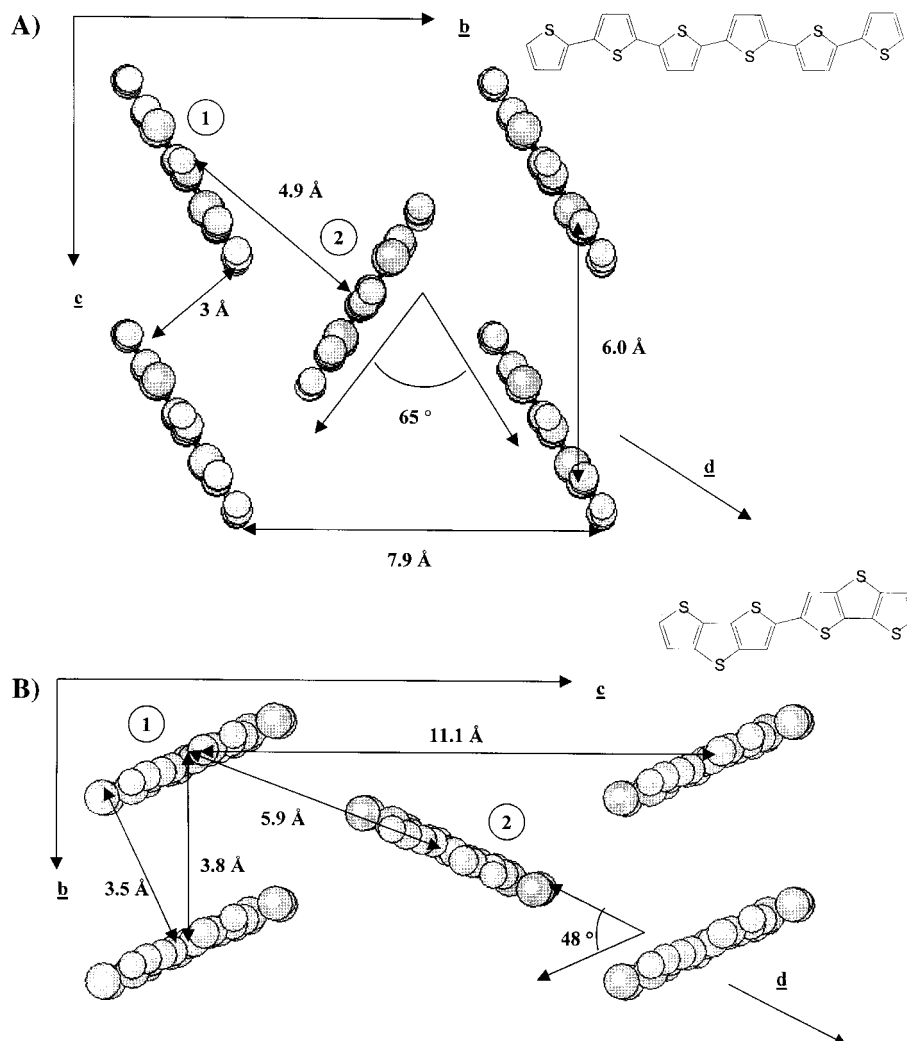


Fig. 1. Lattice parameters within the *bc* layer of crystalline 6T (A) [13] and BDT (B) [14]; labels 1 and 2 refer to the two inequivalent molecules of the unit cell. The full chemical structure of the two compounds is also given.

molecular orbital)/LUMO (lowest unoccupied molecular orbital) levels of the individual oligomer chains. Clusters are considered that contain up to six adjacent molecules stacked in directions giving rise to the strongest intermolecular interactions (see Fig. 1), that is, along the *c* or *b* crystal axes as well as along the *d* axis that connects the inequivalent molecules within the *bc* layer (the inequivalent molecules in the 6T and BDT unit cells are labeled **1** and **2** in Fig. 1); note that since the (interlayer) interactions along *a* in 6T and BDT crystals yield vanishingly small electronic level splittings, they are not discussed in the following.

Figure 2 displays the evolution of the (valence and conduction) bandwidths formed by the interaction of the HOMO and LUMO levels of the 6T and BDT chains as a function of the size of the cluster. The calculated bandwidths evolve linearly as a function of  $\cos(\pi/(N + 1))$ , with *N* being the number of units in the one-dimensional cluster; such an evolution is the one expected in the framework of Hückel or tight-binding theories where the bandwidth is equal to  $4t_{\perp}\cos(\pi/(N + 1))$ , with  $t_{\perp}$  the interchain transfer integral. In the 6T crystal, the bandwidths are very similar along the *c* and *d* directions; the bandwidths saturate rapidly as the size of the cluster grows (which points out that the use of band-structure models is not necessarily required). The conduction bandwidth (splitting of the LUMO levels) is larger than the valence bandwidth (splitting of the HOMO levels). This suggests that in 6T, in the absence of impurities and traps, electrons should be more mobile than holes. These results also demonstrate that intermolecular interactions can lead to a complete breakdown of the quasi-electron-hole symmetry characteristic of the single chains. The calculated bandwidths intimately depend on both the wavefunction of the one-electron levels and the relative locations of the interacting units.

In the following, we discuss the properties derived for the valence band since the hole mobilities have been accurately measured. As the INDO-calculated bandwidths follow a classical cosine relationship with the number of oligomers in the

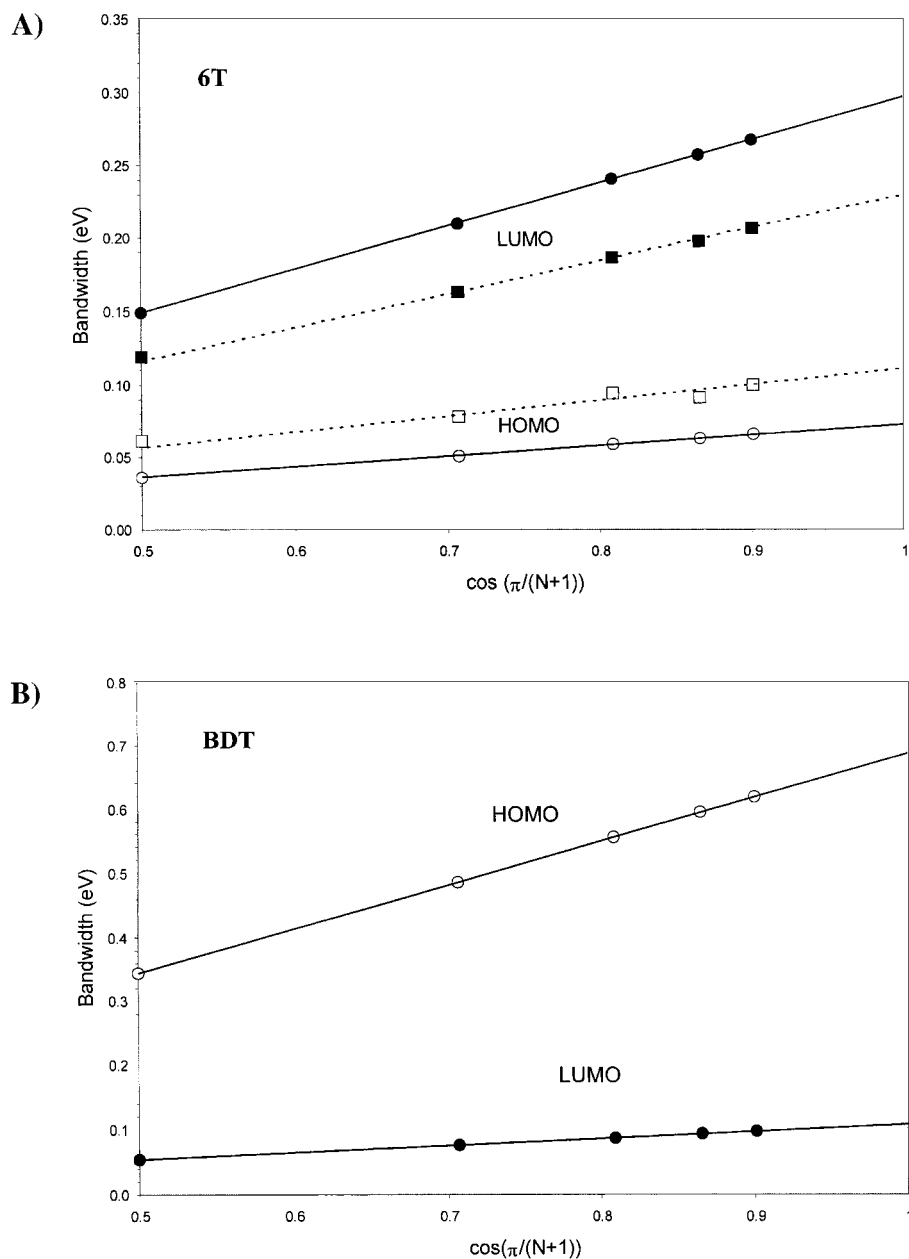


Fig. 2. A) Evolutions of the INDO-calculated bandwidths formed by the HOMO (open symbols) and LUMO (filled symbols) levels of 6T molecules along the *c* (solid lines) and *d* (dashed lines) directions as a function of  $\cos(\pi/(N + 1))$ , with *N* being the number of interacting oligomers. B) Similar evolutions for BDT molecules stacked along the *b* axis; the bandwidths calculated for interacting inequivalent BDT molecules are vanishingly small and therefore not reported in the plot.

cluster, the total valence bandwidth can be estimated within Hückel theory as the energy difference between the most bonding and antibonding interchain patterns in the two-dimensional herringbone packing. When  $t_d$  is larger than  $t_c$  as is the case in the 6T crystal (with  $t_c$  and  $t_d$  corresponding to the interchain transfer integrals along the *c* and *d* axes, respectively), the bandwidth is equal to  $8t_d$ , thus leading to a value of 240 meV. This estimate is in agreement with those inferred from mobility measurements (50–100 meV).<sup>[18]</sup> We calculate a total bandwidth of 328 meV for the crystalline structure of 6T

at high temperature, to be compared to a value of 420 meV provided by extended Hückel band-structure calculations.<sup>[19]</sup>

Transport properties in organic solids<sup>[8–11]</sup> appear to be adequately described by theories based on polaron transport. In such models (which lead to a coherent band motion at very low temperatures and a hopping regime at high temperatures), the squares of the interchain transfer integrals  $t_{\perp}$  between neighboring chains and the amplitude of the electron–phonon coupling are the crucial parameters that govern the hole mobility and the directionality of the transport.<sup>[11]</sup> The interchain transfer integrals in the 6T crystal are calculated at the INDO level to be 18 meV and 30 meV along the *c* and *d* directions, respectively. It is worth stressing that we calculate very similar values for  $\alpha$ -quaterthienyl (4T)<sup>[20]</sup> and  $\alpha$ -octithienyl (8T),<sup>[21]</sup> which have nearly the same chain packing as 6T. These results thus indicate that: i) charge transport in  $\alpha$ -oligothiophenes has a two-dimensional character, in agreement with experimental data,<sup>[22]</sup> and mostly takes place along the *c* and *d* axes within the *bc* layers; ii) the hole mobilities at room temperature (where a hopping regime prevails<sup>[23]</sup>) should be of the same order of magnitude in oligothiophenes ranging from four to eight rings, again in agreement with recent measurements yielding room-temperature mobilities of 0.2 and 0.9 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for high-quality single crystals of 4T and 6T, respectively. These results are consistent with the fact that the reduced strength of electron–phonon coupling as the oligomer size grows<sup>[19]</sup> leads to higher mobilities in longer conjugated segments; however, this does not significantly increase the room-temperature mobilities, thus making the interchain transfer integrals the most relevant parameters to be evaluated. In contrast, the amplitude of the electron–phonon coupling plays a much more critical role at low temperatures in determining the effective bandwidth involved in band-like motions.<sup>[23]</sup>

The situation is strikingly different in the case of the BDT crystal since strong interactions between electronic levels are calculated to be present only for molecules stacked along the *b* crystal axis; the interchain transfer integrals along *b* are estimated to be 172 meV and 27 meV for the HOMO and LUMO levels, respectively. The corresponding values for interacting inequivalent molecules are only on the order of 1.5 meV. In contrast to 6T, the splittings of the HOMO levels are larger than those calculated for the LUMO levels, thus indicating that the holes are intrinsically the more mobile carriers in BDT. Most interestingly, the amplitude of the dominant interchain transfer integrals in the valence band increases by almost one order of magnitude when going from 6T to BDT. Our theoretical results thus predict that: i) the transport in BDT has mostly a one-dimensional character; and ii) the hole mobilities are expected to be much larger than those in 6T; this is in apparent agreement with recent experimental data showing that the room-temperature mobility in BDT thin films ( $20\text{--}50 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)<sup>[15]</sup> is higher than in 4T thin films ( $2\text{--}5 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)<sup>[4,15]</sup> where the electron–phonon coupling is expected to be very similar since the two compounds have the same number of carbon atoms (note that

these experimental values might be biased by grain boundaries and morphological defects that are not accounted for in our calculations); the mobilities reported to date are far from the upper limit value suggested by our theoretical work and hence motivate the synthesis of BDT single crystals.

We now turn to the theoretical characterization of the optical properties of BDT and 6T crystals or thin films. It is here of special interest to investigate the way the lowest excited state of the isolated oligomers evolves in the crystal via formation of an exciton band. The strength of the electronic coupling between the ground state and the lowest excited state in the crystal is a critical parameter for the luminescence quantum yield.

The width of the exciton band has been estimated by means of the INDO/SCI approach in clusters containing up to six interacting 6T chains within a *bc* layer.<sup>[24]</sup> Due to the parallel alignment of the long molecular axes, the lowest excited state of the clusters is calculated to be only weakly coupled to the ground state (as also expected from a simple point-dipole model<sup>[9]</sup>), the whole oscillator strength being concentrated in the upper part of the exciton band. The lack of significant coupling between the ground and lowest excited states rationalizes the significant decrease in luminescence quantum yield when going from solutions to thin films and crystals of 6T.<sup>[7]</sup> When taking explicitly into account the lattice relaxation effects in the excited state (estimated to be on the order of 0.16 eV<sup>[24]</sup>), the INDO/SCI-calculated Davydov splitting in the 6T single crystal (0.34 eV) compares remarkably well to the experimental value (0.32 eV) determined from polarized absorption spectroscopy at 4.2 K.<sup>[24]</sup> The INDO/SCI approach represents a substantial improvement with respect to a traditional point-dipole model, which yields a Davydov splitting larger than 1.2 eV.<sup>[25]</sup>

Figure 3A gives the major results related to the absorption spectra calculated for BDT chains. The lowest absorption peak of the isolated BDT molecule in its solid-state planar conformation is calculated to be 2.67 eV; it is mainly described by a one-electron excitation between the HOMO and LUMO levels. In the two dimers we have considered (formed by two adjacent BDT chains stacked along the *b* axis and by two inequivalent chains), the lowest excited states originate from the mixing of the four one-electron excitations between the highest two occupied and lowest two unoccupied molecular orbitals that are generated upon interaction. The dimers are useful to better apprehend the results obtained on larger clusters.

The lowest excited state of the dimer formed by two inequivalent molecules gives rise to a vanishingly small absorption feature at 2.56 eV with a pronounced charge-transfer character ( $\approx 40\%$ ) as revealed by a CI wavefunction analysis. The intense absorption feature at 2.78 eV has mostly an intrachain character and is blue-shifted with respect to that in the single chain. The Davydov splitting in this dimer is thus estimated to be 0.22 eV. The spectrum obtained for the dimer with two adjacent BDT chains along the *b* axis shows the appearance of an additional absorption feature; this reflects a

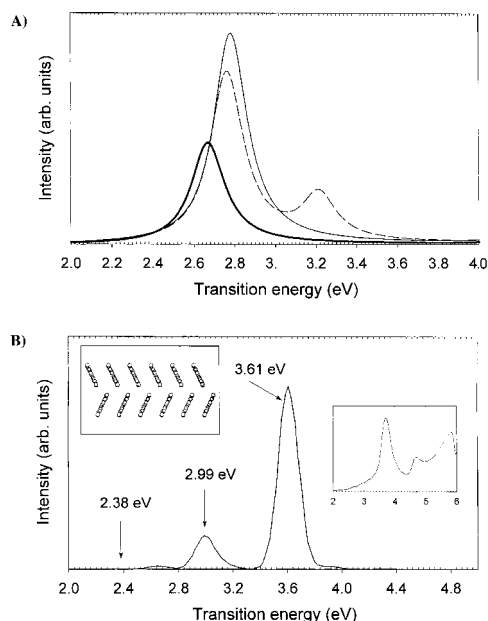


Fig. 3. A) INDO/SCI-calculated absorption spectra for the isolated BDT chain (solid thick line) and for dimers formed by two inequivalent BDT chains (solid line) and by two chains stacked along the *b* axis (dashed line). B) INDO/SCI-calculated absorption spectrum of a cluster containing 12 BDT units, whose structure is illustrated in the upper-left inset. The peaks are convoluted with Gaussian functions whose full-width at half-maximum (FWHM) is set to 0.2 eV. We show in the second inset the experimental spectrum obtained for a BDT thin film, as reported elsewhere [15].

major variation in the strength of the intermolecular forces along the *b* direction, as also evidenced by the calculated interchain transfer integrals. Here, the lowest optically forbidden excited state is located at 2.45 eV while *two* intense absorption features are calculated at 2.76 eV and 3.21 eV. We can thus define two components for the splitting at 0.31 eV and 0.76 eV, respectively. A wavefunction analysis shows that the second intense absorption feature has a dominant *charge-transfer* component; however, its oscillator strength is actually provided by its intrachain component, which is found to increase with the intermolecular interactions; these are here very strong due to the short intermolecular distance, 3.5 Å, along the *b* direction. It is worth stressing that this second intense absorption band cannot be described within traditional excitonic theories. In contrast, in the case of interacting 6T units and inequivalent BDT molecules, the lowest charge-transfer excited state is only weakly optically coupled to the ground state due to the weak interchain couplings.

The present results illustrate that large optical splittings are calculated along both *b* and *d* directions, despite the fact that significant interchain transfer integrals are found only for BDT units stacked along the *b* crystal axis. This demonstrates that in the BDT crystal charge transport is mostly one-dimensional while energy transfer processes can have a three-dimensional character, with the largest optical splittings calculated within the *bc* layer.

In order to confront theoretical and experimental data and ensure the size convergence of the calculated properties, we have considered a large cluster of 12 BDT chains representa-

tive of the crystal, as shown in the inset of Figure 3B.<sup>[26]</sup> The simulated absorption spectrum of the 12-unit cluster, displayed in Figure 3B, is characterized by: i) an intense absorption feature centered around 3.61 eV; ii) a weaker band on the low energy side at 2.99 eV; and iii) the lowest excited state at 2.38 eV with a vanishingly small oscillator strength. The calculated transition energies and relative intensities compare very well to the experimental absorption spectrum of BDT thin films, which show a main absorption at 3.70 eV, a weak band in the energy range between 2.65 and 2.90 eV, and the onset of absorption at  $2.40 \pm 0.20$  eV.<sup>[15]</sup> We estimate from the theoretical results two splitting components at 0.61 eV and 1.23 eV in the BDT single crystal.

To summarize, correlated quantum-chemical calculations on supermolecular structures provide access to quantitative estimates of the parameters governing the carrier mobilities and the luminescence quantum yield in organic thin films. When our approach is applied to crystalline BDT and 6T, the results indicate that the charge transport is highly one-dimensional in BDT while a two-dimensional character prevails in the case of 6T; this is due to the different chain packing between the two crystals. Very interestingly, our results predict a significant increase in hole mobility when going from 6T to BDT; further experimental measurements are required in order to confirm the validity of this prediction. In the two crystals, the lowest excited state is only weakly optically coupled to the ground state, thereby implying that the luminescence quantum yield should be very low. The much stronger intermolecular interactions in the BDT crystal give rise to a main splitting component around 1.2 eV to be compared to a value close to 0.5 eV in 6T (without explicit account of the lattice relaxation effects), in full agreement with experimental data. The present study is being extended to other promising conjugated systems in FETs, such as pentacene and anthradithiophenes.<sup>[27]</sup>

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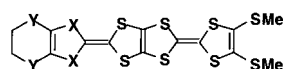
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## TCNQ Complex with θ-Type Donor Arrangement: (TMET-TS-TTP)<sub>2</sub>(TCNQ)\*\*

By Masanobu Aragaki, Hirotada Hoshino, Takehiko Mori,\* Yohji Misaki, Kazuyoshi Tanaka, Hatsumi Mori, and Shoji Tanaka

Radical-cation salts of tetrathiapentalene (TTP) donors are promising organic conductors because of their two-dimensional networks, which are known to favor stabilization of metal-like conductivity down to low temperatures.<sup>[1,2]</sup> Among them, bis(thiomethyl)ethylenedithio-TTP (TMET-TTP) (**1a**) has a strong tendency to form θ-type salts regardless of the counter anions.<sup>[3]</sup> The crystal structure of its TCNQ (7,7,8,8-tetracyanoquinodimethane) salt is not known, but recently we have prepared a selenium analogue, TMET-TS-TTP (**1b**), where the inner sulfur atoms of the ET (bis(ethylenedithio) tetrathiafulvalene) part are replaced by selenium atoms. We



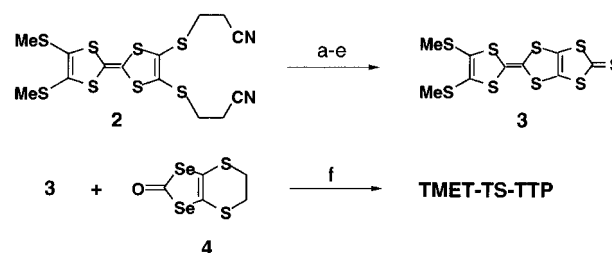
**1a** X=Y=S : TMET-TTP  
**1b** X=Se, Y=S : TMET-TS-TTP  
**1c** X=S, Y=Se : TMES-TTP

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have found that the TCNQ complex (TMET-TS-TTP)<sub>2</sub>(TCNQ) has a θ-type donor arrangement and the TCNQ behaves like an isolated anion. This communication reports the preparation, crystal structure, and electron spin resonance (ESR) investigation of this complex.

TMET-TS-TTP was prepared according to Scheme 1. 6,7-Bis(cyanoethylthio)-2,3-bisthiomethyl-TTF (**2**),<sup>[4]</sup> where TTF



Scheme 1. a) NaOMe (8 equiv.), acetone, room temp., 30 min; b) ZnCl<sub>2</sub>, 10 min; c) Bu<sub>4</sub>NBr, 10 min; d) AcOH, THF, -70 °C to -25 °C, 1 h; e) thiocarbonyldiimidazole, -25 °C to room temp., overnight; f) P(OMe)<sub>3</sub>-toluene (1:1, v/v), 110 °C, 2 h.

is tetrathiafulvalene, was treated with excess (8 mol equivalents) cesium hydroxide monohydrate in acetone, and then with zinc chloride and tetrabutylammonium bromide in methanol. The solvent was then changed to tetrahydrofuran (THF), and a large excess of acetic acid was added at -70 °C. The reaction mixture was allowed to warm up slowly to -25 °C, and an excess of 1,1'-thiocarbonyldiimidazole was added to give a TTF fused with 1,3-dithiol-2-thione, **3** (53 % yield).<sup>[5]</sup> The trimethylphosphite-mediated cross-coupling reaction between **3** and ethylenedithio-1,3-diselenol-2-one, **4**,<sup>[6]</sup> in refluxing toluene afforded TMET-TS-TTP (26 %).<sup>[7]</sup> The cyclic voltammogram of TMET-TS-TTP was composed of four pairs of redox waves at +0.49, +0.66, +0.90, and +1.14 V (vs. Ag/AgCl, in Bu<sub>4</sub>NPF<sub>6</sub>/PhCN). The ΔE (= E<sub>2</sub> - E<sub>1</sub>) value of **1b** was smaller by 0.04 V than that of **1a**.

The temperature-dependent resistivity of some representative salts of TMET-TS-TTP are shown in Figure 1. The conductivity is 1–10 S cm<sup>-1</sup> at room temperature, and behaves like a semiconductor as the temperature is decreased, although many TMET-TTP salts show almost flat temperature dependence down to 200 K. The TCNQ salt of TMET-TTP, however, is an exception: it undergoes a metal-insulator (M-I) transition at around 120 K.

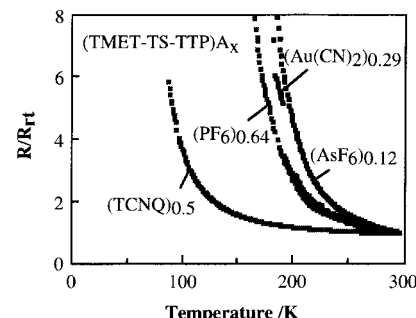


Fig. 1. Temperature-dependent conducting behavior of TMET-TS-TTP salts; A<sub>x</sub> is given beside each curve; x was determined on the basis of energy-dispersion spectroscopy (EDS), except for the TCNQ salt.