

Ab Initio Study of a Molecular Crystal for Photovoltaics: Light Absorption, Exciton and Charge Carrier Transport

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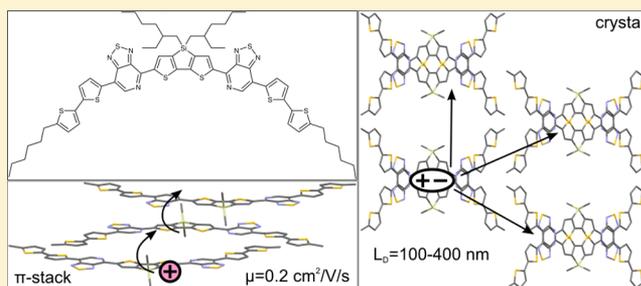
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S Supporting Information

ABSTRACT: Using ab initio methods we examine the molecular and solid-state electronic properties of a recently synthesized small-molecule donor, *p*-DTS(PTTh₂)₂, which belongs to the dithienosilole-pyridylthiadiazole family of chromophores. In combination with the PC₇₀BM acceptor, *p*-DTS(PTTh₂)₂ can be used to fabricate high-efficiency bulk heterojunction organic solar cells. A precise picture of molecular structure and interchromophore packing is provided via a single-crystal X-ray diffraction study; such details cannot be easily obtained with donor materials based on conjugated polymers. In first-principles approaches we are limited to a single-crystallite scale. At this scale, according to our investigation, the principal properties responsible for the high efficiency are strong low-energy light absorption by individual molecules, large exciton diffusion length, and fast disorder-resistant hole transport along π -stacks in the crystallite. The calculated exciton diffusion length is substantially larger than the average crystallite size in previously characterized device active layers, and the calculated hole mobility is 2 orders of magnitude higher than the measured device-scale mobility, meaning that the power conversion “losses” on a single-crystallite scale are minimal.



I. INTRODUCTION

Organic photovoltaic^{1–15} (OPV) devices are of interest in academia and industry because of their potential to provide cost-effective energy generating sources. Organic semiconductors typically are good light absorbers so that the OPV layers are relatively thin (100–200 nm). Optical excitation leads to the formation of a strongly bound electron–hole pair called an exciton. Current is produced through exciton dissociation at heterojunctions between two materials, resulting in the generation of free electron and hole carriers: the electron goes to the material with the higher electron affinity (acceptor), while the hole resides in the material with the lower ionization potential (donor). To increase the donor/acceptor interfacial area and shorten the exciton pathway toward the dissociation, the so-called bulk heterojunction (BHJ) geometry is used,¹⁶ where the donor and acceptor materials form a blend with interpenetrating domains of the two components, each of which directs charge to the corresponding electrode.

From the theoretical point of view, significant first-principles investigations of the processes of light absorption and exciton and charge carrier transport have been published and reviewed.^{17–29} These studies aim to understand the basic physical processes occurring in the active layer thin films and

rationalize the experimental findings down to the molecular scale, with the ultimate goal of providing predictive tools.¹⁷ Despite progress, an accurate theoretical description is still challenging because of the multiscale nature of the problem³⁰ and the inexact details concerning the BHJ structure and the internal organization within the donor and acceptor phases. Even at the single-molecule scale level, ab initio methods are usually limited to density functional theory (DFT), or perturbation theory at most (MP2), because of the size of the system, typically involving hundreds of atoms. Moreover, both DFT and MP2 are prone to errors in describing large π -conjugated systems especially with respect to excited states.^{31–35} Strong vibronic couplings and highly anharmonic torsional modes are typical for materials used in OPVs,^{18,36–38} which significantly complicate the first-principle description. On a larger, mesoscopic scale, the range of available theoretical and experimental methods is limited so that even the geometrical structure of an active layer is difficult to determine with atomic resolution.

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The majority of solution-processed BHJ OPVs studied thus far are based on conjugated polymer donors and fullerene acceptors.^{7,39–41} More recently, small-molecule donors have been reported with efficiencies that are approaching those of their polymeric counterparts.^{42–45} For example, solar cells based on molecular donors containing dithienosilole-pyridylthiadiazole moieties,⁴⁶ such as *p*-DTS(PTTh₂)₂ in Figure 1,

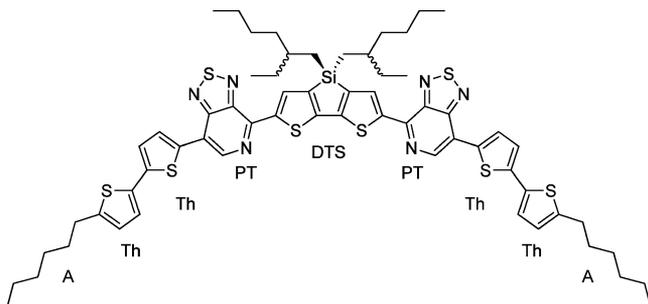


Figure 1. Chemical structure of the *p*-DTS(PTTh₂)₂ molecule: A corresponds to aliphatic chains, DTS, PT, and Th denote dithienosilole, pyridylthiadiazole, and thiophene moieties, respectively.

display power conversion efficiencies as high as 6.7%.⁴⁷ Attractive features of molecular systems include their well-defined structure, ease of functionalization, and the opportunity for purification using standard organic chemistry techniques.⁴⁸ The discrete nature of small molecules allows for a larger breadth of characterization procedures, leading to unprecedented insight into the structural characterization of chromophores within the donor phase. In the case of *p*-DTS(PTTh₂)₂ one observes by transmission electron microscopy formation of crystalline domains, the size of which correlates with device performance.⁴⁷

In this contribution we take advantage of a crystallographically determined structure of *p*-DTS(PTTh₂)₂ to perform theoretical investigation of exciton and charge transport on a single-crystallite scale. Having an experimentally determined picture of the molecular conformation and how these subunits pack within the lattice, our theoretical characterization provides insight into how given particular molecular assembly determines bulk properties. No analogous level of structural insight exists for the narrow band gap conjugated polymer donor materials due to the strict challenge of obtaining polymer single crystals.

The paper is organized as follows. In section II we describe the computational methodology. Section III provides an analysis of the geometry, electronic structure and excitations, and calculations of exciton diffusion and charge carrier mobility. Finally we discuss the trends that emerge, and summarize our results in section IV.

II. COMPUTATIONAL METHODOLOGY

The electronic structure calculations are based on DFT methodology applied to the ground state of neutral and charged molecular systems. Molecular excited states are calculated by taking advantage of the time-dependent DFT (TDDFT) approach. All calculations are carried out with the Gaussian 09 program⁴⁹ using CAM-B3LYP density functional⁵⁰ and the 6-31G* basis set.⁵¹ CAM-B3LYP is a hybrid long-range corrected functional, providing correct description of the neutral excitations³³ and charged states³⁸ in extended π -conjugated systems like the one investigated in this paper.

Description of long-range intermolecular couplings necessitates inclusion of polarization functions into the basis set (6-31G*). Nevertheless, the structure of the modeled absorption spectrum is described sufficiently well with a smaller basis set, 6-31G. To compare calculated and experimentally observed spectra measured in chloroform solution, the solvent effects are taken into account using the conductor-like polarizable continuum model^{52–54} (CPCM) with the dielectric constants $\epsilon_{\text{static}} = 4.7$ and $\epsilon_{\text{optic}} = 2.1$. The static dielectric constant of the studied crystal ($\epsilon_{\text{static}} = 3.8$) was estimated by the Clausius–Mossotti relation. Therefore, the calculations in chloroform can mimic the dielectric effects of the crystalline environment, which is important for estimating the total energy of a charged state.

To study exciton and charge transport in the crystal, we rely on hopping-like models and start with calculating the transition rates between molecules. The assumption of localization of electronic excitations on a single chromophore is an approximation, and more delocalized Frenkel-like excitons⁵⁵ may exist in the crystal (see pp S10–S11 of the Supporting Information for details). Upon our approximation, the exciton-transfer rates between a pair of molecules are calculated by a Förster-like formula:^{19,26,56}

$$w = \frac{2\pi}{\hbar} |V|^2 J \quad (1)$$

where V is the exciton intermolecular coupling and J is the spectral overlap. The methodology of estimating exciton couplings is described on pp S7–S8 of the Supporting Information: it is similar to taking the half-energy split between the two lowest excited states for the molecular dimer^{57,58} but, additionally, is able to treat a case of nonequivalent monomers. The spectral overlap is given by

$$J = \int \rho_{\text{emi}}(E) \rho_{\text{abs}}(E) dE \quad (2)$$

where $\rho_{\text{emi}}(E) \sim I_{\text{emi}}(E)/E^3$ and $\rho_{\text{abs}}(E) \sim I_{\text{abs}}(E)/E$ are normalized (integrated to unity) vibrationally resolved emission and absorption spectral line shapes. For the latter we use the experimentally measured fluorescence excitation and emission spectra,^{59,60} because current DFT methods lack quantitative accuracy in estimating J (see Figure S4 and Table S3 of the Supporting Information).

Charge carrier transfer rates are calculated by the Marcus formula,¹⁸ which for zero field and identical molecules reads

$$w = |t|^2 \sqrt{\frac{\pi}{\hbar^2 \lambda k T}} \exp\left(-\frac{\lambda}{4kT}\right) \quad (3)$$

Here t is the electron-transfer integral, λ is the internal reorganization energy, and T is the room temperature. The internal reorganization energy is calculated from the DFT-derived total energies:¹⁹

$$\lambda = E_{\text{cn}} - E_{\text{cc}} + E_{\text{nc}} - E_{\text{nn}} \quad (4)$$

where E_{cn} is the energy of charged molecule (anion or cation) calculated using an optimal geometry of the neutral molecule, E_{nc} is the energy of the neutral molecule in the geometry optimized for charged molecule, and E_{nn} and E_{cc} are the energies of the neutral and charged molecules, respectively, taken at their corresponding optimal geometries. Transfer integrals are calculated by projecting the Fock matrix of the dimer (obtained from the experimental X-ray crystal geometry) onto molecular orbitals of the respective monomers²⁰ with the subsequent symmetric orthogonalization.⁶¹ The procedure is as

follows: by ab initio DFT we calculate the Fock matrix, \mathbf{F} , and the basis set overlap matrix, \mathbf{S} , for the dimer in the ground state. In addition, we calculate eigenvectors (molecular orbitals) for both monomers in their ground state: they are given as columns of the matrices \mathbf{T}_1 and \mathbf{T}_2 for the first and second monomers, respectively. Then we construct the block-diagonal matrix $\mathbf{B} = \text{diag}(\mathbf{T}_1, \mathbf{T}_2)$ and perform the projection: $\mathbf{F}' = \mathbf{B}^T \mathbf{F} \mathbf{B}$, $\mathbf{S}' = \mathbf{B}^T \mathbf{S} \mathbf{B}$. The elements of the matrices \mathbf{F}' and \mathbf{S}' corresponding to HOMO (LUMO) of both monomers compose the effective two-by-two Hamiltonian for holes (electrons), \mathbf{H} , and the overlap matrix \mathbf{O} . The transfer integral is the nondiagonal element of the matrix $\mathbf{O}^{-1/2} \mathbf{H} \mathbf{O}^{1/2}$.

Finally, exciton diffusion length and charge carrier mobility are calculated by solving the Pauli kinetic equation for the crystal:¹⁹

$$\dot{p}_i(t) = -\tau^{-1} p_i(t) + \sum_j (p_j(t) w_{j \rightarrow i} - p_i(t) w_{i \rightarrow j}) \quad (5)$$

where $p_i(t)$ is the probability for the exciton or charge carrier to be localized on the i th molecule at the moment of time t , w are the calculated transfer rates, and τ is the exciton lifetime (for charges it is infinite). To evaluate the latter, we take the radiative lifetime calculated by the formula²⁶

$$\tau = \frac{3\hbar^4 c^3}{4E^3} |d|^2 \quad (6)$$

where E is the transition energy and d is the transition dipole moment. The explicit formulas expressing the diffusion tensor and diffusion length via transfer rates and crystal geometry are cumbersome and are given on p S12 of the Supporting Information. The mobility tensor, μ , is obtained from the diffusion tensor, D , by the Einstein relation $\mu = eD/(kT)$, where e is the electron charge.

To find the diffusion length we further calculate the mean square displacement tensor

$$\Lambda^{\alpha\beta} = \frac{1}{2\tau} \sum_i R_i^\alpha R_i^\beta \int_0^\infty p_i(t) dt \quad (7)$$

where R_i is the vector in Cartesian coordinates of the i th molecule, provided that initially the exciton was located at the origin. The square root of the trace of Λ gives the exciton diffusion length. Since $\Lambda \sim \tau D$ as $\tau \rightarrow \infty$, our definition of the diffusion length is consistent with the commonly used⁶² formula $(\tau D)^{1/2}$. Because the diffusion is anisotropic, it is more informative to calculate the square root of the eigenvalues of Λ , which gives the exciton diffusion length along the main axes of the tensor Λ . Note that in Monte Carlo simulations mean absolute displacement is usually calculated.²³

The comparison of various ab initio and semiempirical methods within different computational methodologies and the analysis of the assumed approximations have been performed as well and will be presented in subsequent publications.

III. RESULTS AND DISCUSSION

Molecular Geometry. The p -DTS(PTTh₂)₂ molecule, shown in Figure 1, consists of a π -conjugated backbone comprising a central electron-rich dithieno(3,2-b;2',3'-d)silole (DTS) moiety, adjacent [1,2,5]thiadiazolo[3,4-c]pyridine (PT) heterocycles, and terminal hexyl-substituted dithiophene units. Single crystals suitable for X-ray diffraction studies were grown by slow vapor diffusion of acetone into a dichloromethane solution at 4 °C. A view of the resulting molecular structure is

shown in Figure 2. Note that, because the 2-ethylhexyl chains exist as superimposed R/S isomers, the anisotropic displacements

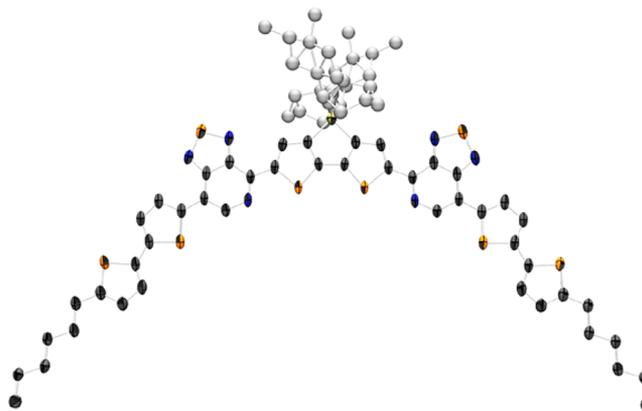


Figure 2. Molecular structure of p -DTS(PTTh₂)₂, as determined by a single-crystal X-ray diffraction study (ORTEP depiction at 50% probability). C, dark gray; Si, yellow; S, orange; N, blue; disordered carbons depicted in lighter gray; H, not shown.

parameters for the carbons could not be determined from the X-ray data. Therefore, the chains were modeled using constrained geometric parameters and isotropic temperature factors as follows: the R and S fragments were modeled by constraining the C–C and C–Si bond lengths and temperature factors to be the same for each fragment, with optimized occupancy being near equal. From Figure 2, one observes that p -DTS(PTTh₂)₂ adopts a distinctive curved shape, as opposed to a more linear geometry.⁶³ A measure of this departure from linearity can be obtained by noting that the angle between the Si bridgehead atom and the centroids in the terminal thiophene rings is 103.9°.

In the crystal p -DTS(PTTh₂)₂ forms stacks, as shown in Figure 3a, in which the orientation of the molecules alternates down the direction of the stacks. The π – π distance is approximately 3.5 Å within the stack (measured as the distance between the average planes of the molecules), with a slip-stack arrangement between the two molecules. When viewed along the stacking directions one observes a two-dimensional close-packed lattice as shown in Figure 3b and schematically cartooned in Figure 6a.

To test the computational methods and elucidate the influence of the molecular environment, we compare experimental (crystal) and computed (in vacuo and in solution) geometries of the conjugated framework. The mean square deviation is 0.01 Å for bond lengths, and 0.08° for bond angles. The global structure of the conjugated framework is compared using the “nonplanarity” parameter, which is the mean square deviation of the distances to the plane that minimizes the deviation (least-squares plane or orthogonal distance regression plane). For the optimized geometry the value of the nonplanarity is 0.19 Å in vacuo and 0.20 Å in chloroform with $\epsilon = 4.7$. In the experimental X-ray crystal geometry, this value is 0.05 Å. The difference shows that the molecules are more planar within the crystal lattice due to the π -stacking. These features are relevant for the observed red shifts in the absorption spectrum when transitioning from solution to the solid state.⁶⁴ Note also that, because of the shorter conjugation length, this effect is expected to be smaller than in conjugated

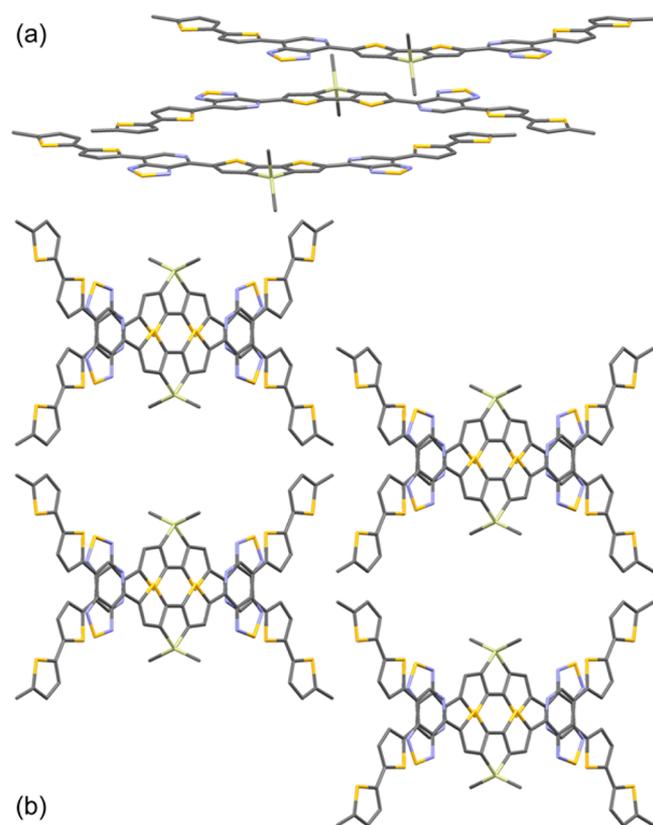


Figure 3. (a) Side view of the π -stack in the crystal. Hydrogens and aliphatic chains are not shown. The stacking period is two molecules. (b) The crystal viewed along the stacking direction. C, dark gray; Si, light green; S, yellow; N, blue; H, not shown.

polymers, e.g., various forms of polythiophene for both crystal versus solution⁶⁵ and regioregular versus regiorandom forms.⁶⁶

Electronic Structure and Analysis of UV–Vis Spectra in Solution. For the analysis of electronic excitations and carrier transport, three molecular orbitals (MOs) are essential: HOMO, LUMO, and LUMO + 1. The energy splitting of the latter two orbitals is 0.3 eV. The rest of the MOs lie about 0.4 eV below and 1 eV above these three. The HOMO is delocalized over the entire conjugated framework, except for the five-membered rings of the PT units, see Figure 4a. Two LUMOs show localization mainly on the two PT units. Electronic structure of a single molecule does not differ significantly for the geometries considered: as-in-crystal, optimized in vacuo, or optimized in solution (see Figure S1 of the Supporting Information).

The calculated UV–vis absorption spectra are shown in Figure 5 together with the experimental absorption and emission spectra taken in chloroform solution. The overall agreement between experimental and calculated absorption spectra is very good. The lowest optically active band gap transition is polarized along the long axis of the molecule. Our calculations interpret a shoulder on the blue side of the fundamental absorption peak as a second electronic transition (vs conventional assignment of this shoulder to vibronic transitions). Its transition dipole moment is perpendicular to the long axis of the molecule and, thus, is much smaller than the first state transition dipole moment because of the short extent of the wave function in this direction (see Table 1 and the discussion below). Finally, we assign the broad high-energy peak in the 3–4 eV range to multiple electronic transitions. Individual excited states can be further analyzed using natural transition orbitals (NTOs),^{67,68} which give a simple orbital picture of the results of TDDFT calculations, see Table 1. In

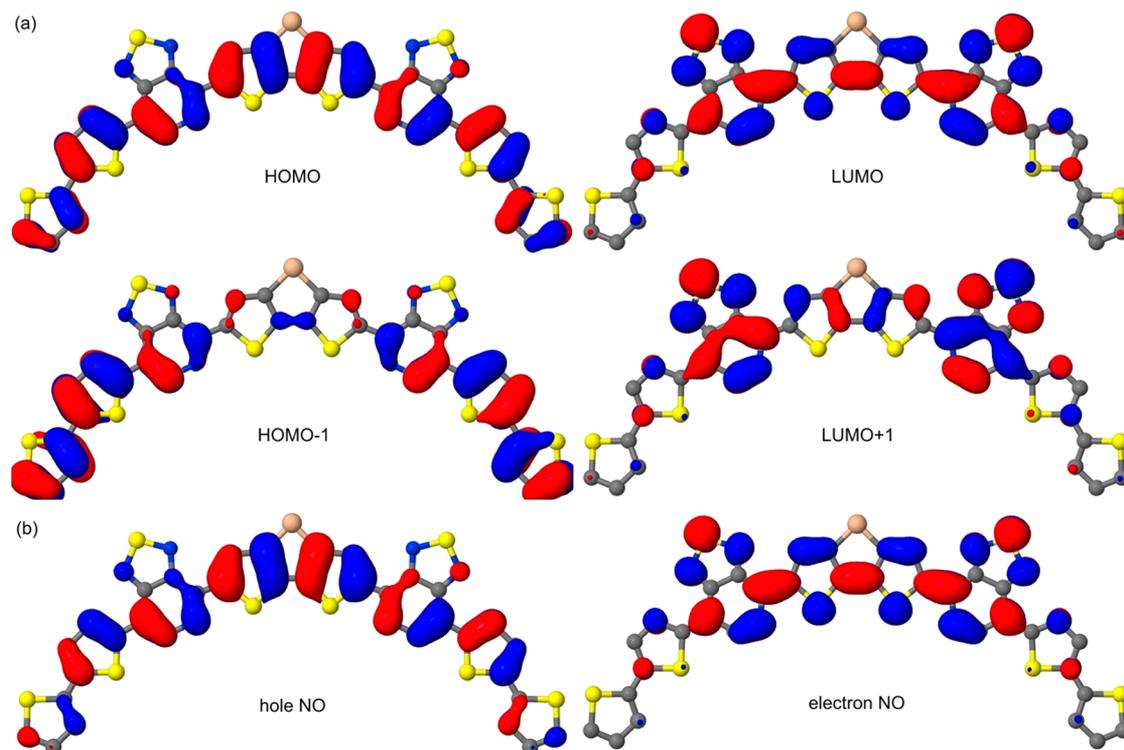


Figure 4. (a) Frontier molecular orbitals of *p*-DTS(PTTh)₂. Hydrogens and aliphatic chains are not shown. (b) Half-filled natural orbitals for electron and hole polarons, obtained for optimized anion and cation species.

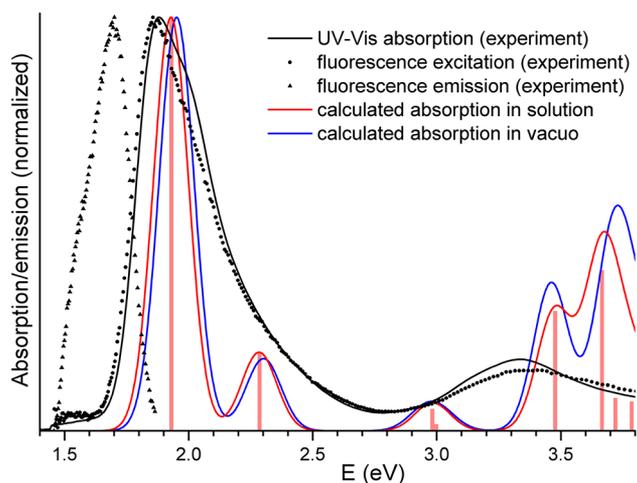


Figure 5. Emission and absorption spectra of *p*-DTS(PTTh₂)₂ molecule. Experimental spectra are obtained in chloroform solution. Calculated spectral lines (CAM-B3LYP/6-31G) are broadened by a Gaussian function with a line width of 0.05 eV. Individual transitions are shown by bars whose heights are proportional to the oscillator strengths of the transitions.

this analysis each electronic transition is represented in terms of two orbitals (electron and hole).

Now we focus our discussion on the first two transitions constituting the lowest-energy absorption band in the experimental spectrum (Figure 5). By comparing the hole and electron NTOs in Table 1 with HOMO and LUMOs in Figure 4a we see that the first transition is essentially HOMO–LUMO transition and the second transition is HOMO–LUMO + 1 transition. The small difference between the hole NTO and the HOMO is due to a slight hole localization that is expected for such sufficiently long conjugated molecule. LUMOs are largely localized on the PT units; therefore, no further localization for the electron NTO is expected except possible symmetry breaking with complete electron localization on one PT unit. Both transitions have partial charge-transfer character with the PT unit acting as an acceptor for given optical transitions from the ground to excited states. A similar picture applies to NTOs describing higher excited states: every optical transition leads to a partial electron transfer from the peripheral rings or the central DTS unit to the two PT groups, in accordance to common chemical intuition.

The polarization of electronic transition using the orbital picture can be rationalized as follows. First, note that the conjugated frameworks themselves have an approximate C_{2v} symmetry; the HOMO and two LUMOs have approximate a_2 , b_1 , and a_2 symmetries, respectively (a_2 is c_2 symmetry and b_1 is σ_{perp} symmetry). According to this approximate symmetry, the transition dipole for the HOMO–LUMO transition is oriented along the conjugated framework (b_2 symmetry), while the dipole for the HOMO–LUMO + 1 transition is oriented perpendicular to the molecular long axis (a_1 symmetry). The rest of the MOs are relatively isolated. Therefore, we expect to see an isolated absorption peak composed of the lowest-energy strong HOMO–LUMO and the higher-energy weak HOMO–LUMO + 1 transitions in the polarization spectroscopy of aligned samples.

Analysis of Fluorescence Excitation/Emission Spectra.

To estimate the spectral overlap and other parameters of the exciton transport we analyze the shape of the emission and first

absorption bands determined by the fluorescence spectroscopy (Figure 5). To fit the experimental spectra, we assume the displaced harmonic oscillator model, consistent with the results of ab initio calculations (see Figures S2 and S3 of the Supporting Information). The spectral shape of the first absorption band in Figure 5 is formed by the vibrational broadening of the two electronic transitions. Each vibronic transition is further broadened mainly by external factors such as inhomogeneous broadening. We assume that this broadening is small compared to the vibronic progression, and describe it by the Gaussian function, so that each vibronic transition has Gaussian line shape with the same dispersion σ .

The spectra of large molecules are vibrationally broadened well enough so that their 0–0 edge can be approximated by the Gaussian shape:

$$\rho(E) = \frac{1}{\sqrt{2\pi(2\lambda'kT + \sigma^2)}} \times \exp\left(-\frac{(E - E_{00} \pm \lambda')^2}{4\lambda'kT + 2\sigma^2} - S''\right) \quad (8)$$

Here λ' is the effective reorganization energy due to the environment and classic intramolecular vibrational modes (whose energy is much smaller than the temperature), S'' is the effective Huang–Rhys factor for the “quantum” vibrational modes (collective coordinate for the rest of the modes), σ is an inhomogeneous line broadening, E_{00} is 0–0 transition energy, the upper sign at λ' is for emission, and the lower one is for absorption. This formula is detailed on p S2 of the Supporting Information and corresponds to the 0–0 transition description in the Bixon and Jortner model.^{19,69} The results of the experimental spectra fits and cross-checks (see Figure S5 and Table S3 of the Supporting Information) show that the chosen model is adequate, and the fitting parameters are $\lambda'_{\text{abs}} = 0.11$ eV, $\lambda'_{\text{emi}} = 0.07$ eV, $S''_{\text{abs}} = 0.4$, $S''_{\text{emi}} = 0.2$, $\sigma = 0.04$ eV, $E_{00} = 1.75$ eV. The inhomogeneous broadening is small compared to $(2\lambda'kT)^{1/2} = 0.1$ eV; therefore, the experimental line shapes can be used for the spectral overlap estimate.

The spectral overlap, J , is calculated as follows: the lower estimate is obtained by using the Gaussian shape (formula 8) with the above-determined parameters but no inhomogeneous broadening ($\sigma = 0$). The upper estimate is obtained with $\sigma = 0.04$ eV, assuming that the inhomogeneous broadenings of individual molecules are independent. This gives a calculated J of 0.4–0.6 eV⁻¹, and the direct convolution of the measured spectra gives a value, 0.6 eV⁻¹, similar to the calculated upper bound value. When using the obtained spectral overlap value for calculating exciton-transfer rates in the crystal, we assume that the spectral broadening in the crystal is not larger than in the solution.

To determine the exciton transport regime we need to evaluate the corresponding reorganization energy, which can be estimated by the formula

$$\lambda = \lambda'_{\text{emi}} + \lambda'_{\text{abs}} + (S''_{\text{emi}} + S''_{\text{abs}})\hbar\omega'' \quad (9)$$

where ω'' is the effective frequency for the quantum modes. The latter are typically C=C stretching modes^{27,70} with $\hbar\omega'' \sim 0.2$ eV; hence, $\lambda = 0.3$ eV. The alternative estimate based on the global analysis of the spectra (formula S5 of the Supporting Information) gives the same value.

Exciton Transport. From the crystal structure in Figure 3b, one can build a simplified picture of how the stacks organize

Table 1. Natural Transitions Orbitals for the First Five Excited States of the Molecule in Chloroform Obtained from TD-CAM-B3LYP/6-31G Calculations^a

parameters	hole NTO	electron NTO
E = 1.94 eV f = 1.83 NTO w = 0.84 CI w = 0.40 HOMO-> LUMO		
E = 2.29 eV f = 0.35 NTO w = 0.61 CI w = 0.30 HOMO-> LUMO+1		
E = 2.99 eV f = 0.10 NTO w = 0.50 CI w = 0.24 HOMO+HOMO-2 ->LUMO+1		
E = 3.00 eV f = 0.03 NTO w = 0.56 CI w = 0.25 HOMO-2-> LUMO		
E = 3.49 eV f = 0.54 NTO w = 0.53 CI w = 0.25 HOMO-> LUMO+2		

^aNotations: “*E*” is the transition energy, “*f*” is the respective oscillator strength, “NTO w” is the weight of the given NTO pair in the corresponding transition density matrix, “CI w” is the weight of the Kohn–Sham orbital pair in the corresponding transition density matrix. The latter two molecular orbitals are identified in the following two lines.

themselves, as shown in the cartoon representation in Figure 6a. A map depicting the largest intermolecular exciton couplings is shown in Figure 6b. Because excitons can move via the long-range Förster transfer mechanism, their transport does not depend strongly on the local intermolecular structure. As a result, we see in Figure 6b a more or less isotropic distribution of couplings. The strongest coupling, 63 meV (500 cm⁻¹), is between the nearest neighbors in the π -stack. At large intermolecular separations compared to the monomer’s size we expect to observe an inverse cubic dependence of couplings on the distance between the monomers due to a dipole–dipole type of interaction. In fact, even for hundreds of dimers we

calculate (all dimers within a given maximum 30 Å contact distance) the observed distance dependence is much smaller (Supporting Information Figure S7). This is because the molecules are large, 26 Å without aliphatic chains, and of complex shape.⁷¹ This justifies our approach to evaluate excitonic couplings from the splitting of excited states in a dimer, compared to a less accurate point–dipole approximation. In comparison to other organic conjugated systems, our estimated absolute values of the couplings are moderate: couplings exceeding 100 meV are not rare.^{22,26,57}

The above-calculated couplings should be corrected for the effects of the crystalline environment.⁷¹ At large intermolecular

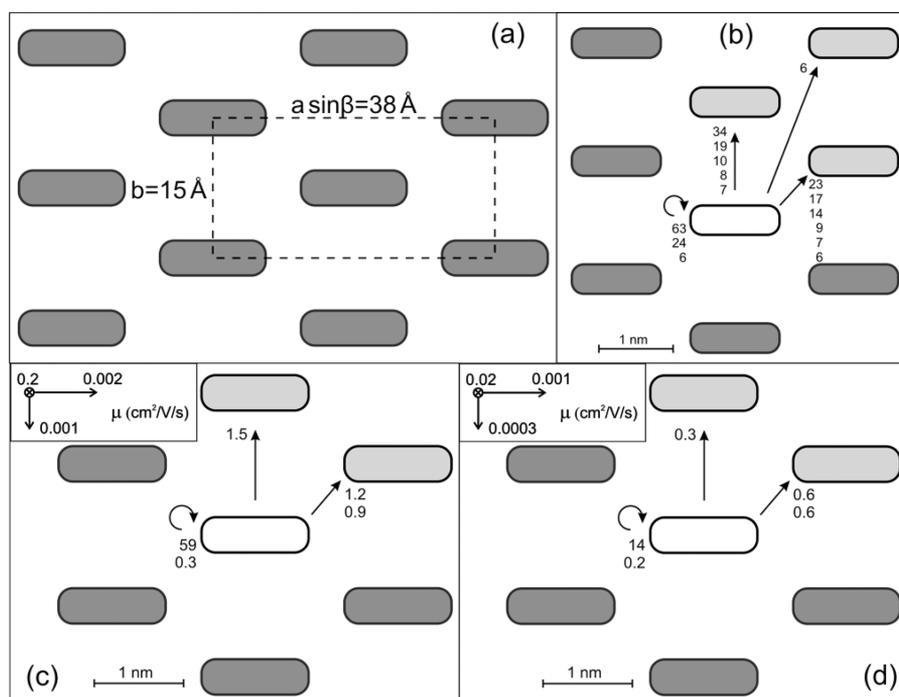


Figure 6. (a) Cartoon version of Figure 3b summarizing the important features of the crystal lattice. Here π -stacks run perpendicular to the figure plane and are represented as the rounded rectangles. The on-plane projection of the monoclinic unit cell is shown as the dashed rectangle. The stacking direction is along the c -axis. (b) Excitonic intermolecular couplings (absolute values in meV) are shown for all dimers coupled stronger than 5 meV. All molecules are equivalent. Some dimers are also equivalent: the dark gray rectangles (π -stacks) are symmetry-equivalent to the light gray ones. The circled arrow denotes the intrastack couplings, e.g., 63 meV is for the nearest neighbors in the π -stack, 24 meV is for the next nearest neighbors, etc. Similarly, there is a number of interstack dimers for each pair of stacks (the straight arrows); the corresponding couplings are listed in the descending order. (c) Hole-transfer integrals (meV) shown for all dimers coupled stronger than 0.1 meV. The calculated hole mobilities along the main axes of the mobility tensor are shown in the inset. (d) Same as panel c but for electrons.

distances, these effects reduce the couplings by the squared refraction index of the crystal. Unfortunately the crystal absorbs light at the frequencies of interest, severely complicating the estimation of this index. At small distances the effects are even more complicated,⁷¹ though the *ab initio* calculations for small multimers (Table S4 of the Supporting Information) show that the dimer-in-vacuo approximation gives correct couplings for these systems.

Because the largest excitonic coupling, 63 meV, is much smaller than our evaluated internal reorganization energy, $\lambda = 0.3$ eV, we expect that relaxed excitons will move via the hopping mechanism.²² The calculated largest intermolecular transfer rate, $1/60$ fs⁻¹, is comparable with intramolecular relaxation rates,^{72,73} implying that the hopping is not purely incoherent. More accurate analysis of the transport regime is given on pp S10–S11 of the Supporting Information. The estimated by formula 6 exciton radiative lifetime is 2.5 ns.

The calculated exciton diffusion length of about 100–400 nm depends on the direction of diffusion in the crystal, with the largest diffusion length being along the π -stack. Note that this estimate is valid only for an idealized crystal. In fact, nonradiative processes and traps decrease the exciton diffusion length substantially.⁶² However, if the concentration of defects (except for the grain boundaries) is low enough to have a majority of crystallites free of deep traps, we can state that the relaxed excitons are able to sample the entire crystallite because the typical crystallite size in thin films, 20–30 nm,⁴⁷ is much smaller than the estimated exciton diffusion length. Practically, this means that photogenerated excitons can be delivered to the charge-separating interface with 100% efficiency for trap-free

crystallites. This is true if the crystallites are surrounded by fullerene within the BHJ blend, which may or may not be the case in a real device layer.

Charge Carrier Transport. Maps of the intermolecular transfer integrals for holes and electrons are shown in Figure 6, parts c and d, respectively. Because transfer integrals depend exponentially on the contact distance between the underlying conjugated bases, they are essentially nonzero only for the nearest neighbor molecules. Transfer integrals between the π -stacked molecules are 1–2 orders of magnitude larger than those for other dimers. Therefore, the transport of charge carriers occurs mainly along the π -stack.

The calculated internal reorganization energies are 0.43 and 0.36 eV for the hole and electron polarons, respectively, implying that we are in the regime of strong electron–phonon coupling and the small-polaron hopping model is the correct approximation. The natural orbitals (NO) obtained for the cation and anion species are shown in Figure 4b: the electron NO coincides with the LUMO, whereas the hole NO is slightly more localized compared to the HOMO. We have observed the same picture for the NTO analysis of the excitonic transition. Comparison of calculated NOs and HOMO/LUMO justifies our assumption of the latter being states of electron and hole on a single molecule, central to the charge transport calculations.

Calculated transfer rates between π -stacked molecules are 1.6 ps⁻¹ for holes and 0.2 ps⁻¹ for electrons. These values are slower than intramolecular relaxation rates for charges. The largest transfer rates across the stack are 2–3 orders of magnitude smaller.

The calculated hole mobility along the π -stack is $0.2 \text{ cm}^2/\text{V/s}$. This value is 2 orders of magnitude smaller than the highest experimentally reported mobility for molecular crystals²¹ (e.g., pentacene). However, this single-crystal mobility is about 2 orders of magnitude larger than the measured mobility in thin films of optimized p -DTS(PTTh₂)₂/PC₇₀BM blends.⁴⁷ For the pristine p -DTS(PTTh₂)₂ thin films cast from a solution the measured hole mobility in the saturation regime is $0.1 \text{ cm}^2/\text{V/s}$.⁴⁷ A crude estimate of this high-field mobility for a crystal can be obtained by omitting the exponent in formula 3. Thus calculated value is again 2 orders of magnitude larger than the measured thin film mobility. In contrast to excitons, we expect that holes are efficiently transported through the crystallites only along the π -stacks (in the absence of any traps).

In the crystal the effects of thermal disorder should not influence hole transport along the π -stack due to the delocalization of the HOMO over the conjugated framework combined with the large intermolecular contact area. LUMO states are localized on PT units; therefore, the thermal disorder is expected to suppress electron mobility. Across the stack transport proceeds via point contacts; therefore, those transfer integrals must be thermally averaged.⁷⁴

Finally, we can compare the calculated ionization potential (IP) and electron affinity (EA) with those determined by cyclic voltammetry.⁴⁷ The definitions of these quantities are uncertain to the amount of the geometry relaxation energy (i.e., whether the neutral or charged states are vibrationally relaxed or not).⁷⁵ Also the results of cyclic voltammetry measurements are influenced by the details of the process, in particular by interfacial dipole built up on the electrodes, solvent effects, and possibly the vicinity of charge compensation ions.⁷⁶ The adiabatic limit, i.e., $\text{IP} = E_{\text{cation}} - E_{\text{ground}}$ and $\text{EA} = E_{\text{ground}} - E_{\text{anion}}$ with fully relaxed geometries, seems to be more appropriate for “slow” cyclic voltammetry. In the usually plotted energy-level diagrams, “HOMO” and “LUMO” levels correspond to $-\text{IP}$ and $-\text{EA}$ values, respectively. The calculated IP, 5.3 eV (in solution), is in agreement with the cyclic voltammetry estimate, 5.2 eV. The calculated EA is 2.9 eV, whereas the cyclic voltammetry estimate is 3.6 eV; the difference is within the uncertainty limits of the latter method⁷⁷ (the measured reduction onset referenced to Fc/Fc^+ is -1.3 V). Note that in the opposite, fixed geometry limit, $\text{IP} = 5.5 \text{ eV}$ and $\text{EA} = 2.7 \text{ eV}$.

IV. CONCLUSIONS

In summary, the electronic properties of p -DTS(PTTh₂)₂ in a variety of environments were investigated using DFT approach. Of particular relevance to the function of OPVs is that the structural information is obtained from X-ray diffraction studies of crystals similar to those observed in the donor domains of high-efficiency OPVs. It is difficult to anticipate obtaining such structural details with the more widely used conjugated polymer donor materials due to their higher amorphous content and inability to obtain suitable single crystals. Our DFT and TDDFT calculations show that at the molecular level the electrons in p -DTS(PTTh₂)₂ are mostly localized on the two central PT units, and we observe that the LUMO, electron NTO, and electron NO are visually identical. The HOMO is delocalized over the entire chromophore, and we observe some localization of exciton and hole polaron such that hole NTO and hole NO are visually identical.

The first absorption peak corresponds to a HOMO–LUMO transition with the transition dipole oriented along the long axis

of the conjugated framework. Exciton transport is nearly isotropic in the crystal. The calculated diffusion length of the excitons exceeds the typical size of crystallites experimentally observed in the OPV devices. Hole transport occurs mainly through the π -stacks with a moderate computed mobility. The transport along the stack is not influenced by the thermal disorder due to the large intermolecular contact area. Therefore, we can conclude that there is no “power conversion efficiency loss” on the scale of a single crystallite, provided that it is surrounded by the fullerene phase. We recognize that the reality in a real BHJ active layer is different; for example, there may be amorphous domains of p -DTS(PTTh₂)₂ or incompletely phase-separated domains. These imperfections may account for the losses in efficiency because of their influence on charge separation process⁷⁸ and charge transport on a mesoscale, for example, because of grain boundaries, interfaces, and incomplete percolation pathways.

Overall, our investigation shows that the high power conversion efficiency of p -DTS(PTTh₂)₂ is not due to a “special” electronic feature, but rather due to a combination of multiple properties, including broad UV–vis light absorption, the combination of several donor- and acceptor-rich components on a single molecule giving rise to charge-transfer characteristics and efficient intermolecular charge transport, ability to form crystallites of the correct size, the ease of achieving high levels of chemical purity, and the optimized morphology of the active layer. A few concluding remarks can be made within the context of designing new small-molecule donors for improving the solar cell efficiency. Larger conjugated backbones lead to lower energy absorption and higher molar extinction coefficients. Crystalline domains allow for exciton “delocalization” and additional red-shifts of optical absorption spectra. It is also reasonable that larger intrastack contact area makes the charge transport more disorder-resistant. Smaller intrastack separation would conversely increase the hole-transfer integrals between the π -conjugated stacks. Tightly packed stack geometry suppresses molecule buckling and, as result, increases the spectral overlap for excitons and decreases the reorganization energy for holes.

In the current contribution we focus on the transport properties in the crystalline domains of a small molecule, since it has been experimentally observed that these small-molecule domains dominate thin films in OPV devices. Recent theoretical work has attempted to evaluate the effects of conformational disorder for frontier orbital delocalization and for charge/exciton delocalization and transport.^{30,79} We will use similar methodologies to assess the impact of interfaces between crystalline grains and amorphous regions on the transport and photovoltaic device performance in future studies.

■ ASSOCIATED CONTENT

Supporting Information

Plots of molecular orbitals, details on displaced harmonic oscillator model, ab initio calculations for spectra, analysis of experimental spectra, details on exciton couplings, analysis of exciton transport regime, solution of kinetic equation, crystal synthesis, and structural characterization including the cif file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

BHJ, bulk heterojunction; CI, configuration interaction; DFT, density functional theory; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; MO, molecular orbital; NO, natural orbital; NTO, natural transition orbital; OPV, organic photovoltaic devices; TDDFT, time-dependent density functional theory

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