Enhancing thermoelectric figure-of-merit by 1D electrical transport in bulk Bis-Dithienothiophene molecular crystal

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The use of thermoelectric effect to convert waste heat into electricity holds the promise for future clean energy solutions1–3. Searching for efficient and low-cost thermoelectric materials, especially through phonon-engineering in nanostructures, is the focus of current ongoing research activities5–9. So far, most of the work focuses on inorganic materials1,3. Here, through first-principles electronic structure calculation and classical molecular dynamics simulation, we show that, determined by the nature of its chemical bonding, the bulk π-π stacking Bis-Dithienothiophene molecular crystal (BDTMC) naturally has both one-dimensional electrical and phonon-glass-like thermal transport properties. While these two important ingredients of highly efficient thermoelectric material can only be achieved through complicated engineering in traditional inorganic materials, here they are inherited from the chemical nature of the molecular crystal. We obtain a maximum room-temperature $ZT$ of 1.48. These results illustrate the promising potential of BDTMC and similar π-π stacking molecular crystals as efficient thermoelectric material.

I. INTRODUCTION

The thermoelectric efficiency of a material is characterized by the dimensionless figure of merit $ZT = \sigma S^2T/(\kappa_e + \kappa_{ph})$, with $S$ the Seebeck coefficient, $\sigma$ the electrical conductivity, $\kappa_e$ the electron thermal conductivity, $\kappa_{ph}$ the phonon thermal conductivity, and $T$ the temperature. The optimization of $ZT$ is a highly nontrivial task, e.g., the electrical conductivity and the electron thermal conductivity are, in many cases, related by the Wiedemann-Franz law. Different strategies have been proposed to increase the $ZT$ value. In their seminal work, Hicks and Dresselhaus proposed to increase the $S$ utilizing the sharp change of electrical density of states (DOS) in low dimensional structures5,6, such as semiconductor quantum wells, quantum wires, quantum dots, and single molecular devices3,4. Another approach is looking for electron-crystal-phonon-glass materials by phonon engineering (phononics)10. The idea is to reduce the phonon thermal conductivity while keeping the electrical conductivity intact, due to the different time and length scales of electrons and phonons1. Recently, phonon engineering is used in low dimensional structures, like silicon nanowires, to drastically increase $ZT$7–9. Thus far, the main focus of the research community is inorganic materials, including bulk semiconductors (Bi$_2$Te$_3$, PbTe or SiGe)2,11, perovskites12 and tailored phononic crystals13 or alloys. Recently, a $ZT$ value of 2.6 has been realized in SnSe14.

However, most high-$ZT$ materials contain low abundance elements and are hard to fabricate. Comparing to inorganic materials, organic crystals are light-weighted, low-cost, and flexible. Due to the weak bonding between different molecules, organic crystals have natural low thermal conductivity15,16. Recent experimental progress has resulted in several orders of magnitude increase of $ZT$, from $10^{-3}$ to $10^{-2}$17,18 to 0.4219,20. Moreover, it is now possible to design and modulate the transport characteristics of organic structures15. Among them, π-π stacking molecular crystals have proved their superior electronic transport properties along the development of organic field-effect transistors21. Interestingly, the electronic transport properties can be controlled by tuning π-π stacking angle and distance21,22. Despite the intense study of electronic transport properties, the thermoelectric transport in π-π stacking molecular crystals has not been well understood16,23.

In this work, we study the thermoelectric transport in an organic π-π stacking Bis-Dithienothiophene molecular crystal (BDTMC). Recently, it has been shown that the BDTMC has a superior performance as materials for organic field effect transistor21,25. The electronic transport properties are studied employing the semi-classical Boltzmann transport theory. For the electronic structure, we use a simple one-dimensional tight-binding model that is validated by comparing with Density Functional Theory (DFT) calculation. Meanwhile, the lattice thermal conductivity is calculated using the classical molecular dynamics (MD) simulation. We show that, quasi-one-dimensional (Q1D) electronic transport and phonon-glass-like thermal transport are realized at the same time in bulk BDT molecular crystal, which suggests a great thermoelectric potential for π-π stacking organic molecular crystals.

II. RESULTS AND DISCUSSION

A. Electronic structure.

Figure 1(a) shows the relaxed structure of the BDTMC. It forms a triclinic Bravais lattice, with two molecules within one primitive unit cell, shown in dashed
FIG. 1. The lattice and DFT band structure. (a) The relaxed structure of the BDT crystal along different directions. The lattice vectors are: \(a_1=(16.82, 0.087, 0.015) \text{ Å}, a_2=(16.40, 3.85, 0.015) \text{ Å}, a_3=(-2.08, -0.24, 10.68) \text{ Å}\). The \(y\)-direction is approximately perpendicular to the molecular plane. (b)-(c) DFT band structure and density of states (DOS) of the BDT crystal. The energy zero is set to the top of the valence band. The reciprocal space coordinates of high-symmetry points are \(G=(0, 0, 0), B=(-0.5, 0.5, 0), D=(0.5, 0.5, 0), Z=(0, 0, 0.5)\), in unit of the reciprocal lattice constants. The red dots represent the bands fitted using one-dimensional band dispersion \(\varepsilon \sim -2t \cos(kL_0)\), with \(t=-0.2, -0.2\) eV for the two valence bands, and \(-0.05, -0.08\) eV for the two conduction bands (see text for details). (d) Charge density distribution of the two nearly degenerate HOMO orbitals in one isolated unit cell. They are localized in each molecule, and form the two valence bands in the lattice structure. (e) Corresponding LUMO orbitals forming the conduction bands.

lines. The conduction (CB), valence band (VB) structure and DOS are shown in Fig. 1(b) and (c). We observe a strong band dispersion along \(y\) direction, G-B-G, comparing to other directions. This indicates a large overlap of \(\pi\) orbitals between molecules along \(y\) direction, due to the small angle between \(y\) and the \(\pi-\pi\) stacking (\(\pi\)) direction. The band structure along \(y\) is well reproduced by a fitting using the dispersion of 1D tight-binding model (red dots). Model details are given in the supporting information (SI).

Due to a small electronic overlap between molecules in the same unit cell, the conduction and valence bands come in pairs, each mainly localized in one molecule. By comparing the charge distribution of the bands with the electronic states of the isolated molecule pair, we find that the VB and CB are simply formed by the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of each molecule, respectively [Fig. 1 (d) and (e)]. The strong anisotropy in band dispersion suggests the formation of Q1D band structure along \(y\) direction. This is further supported by the von-Hove-like high DOS near the band edges [Fig. 1(c)]. Hereafter, we focus on the electrical properties along \(y\) direction.

Although the transport mechanism in organic crystals is still under active debate, due to the large band dispersion, we believe that band-like transport theory is appropriate along \(y\) direction. Based on the band structure obtained from Vienna Ab-initio Simulation Package (VASP)\(^{26}\), we use the semi-classical Boltzmann transport theory in the constant relaxation time \((\tau)\) approximation to calculate the band structure contribution to the transport coefficients, e.g., \(\kappa_e/\tau, S^2\sigma/\tau\). The BoltzTrap code is used for this purpose\(^{27}\). Rigid band approximation is used to relate the Fermi level \((E_f)\) position with the electron/hole doping concentration [Fig. 2(a)]. The weak dependence of \(E_f\) on doping within three decades is due to the von-Hove-like DOS at the band edges. Thus, similar to Q1D structure, we expect a high Seebeck coefficient shows up in the bulk molecular crystal. The DFT result is further compared with a 1D model calculation using the parameters obtained from fitting the band structure (Details in SI Sec. S1). We find excellent agreement between the two approaches near the band edges [Fig. 2(b-c)].

B. Electrical transport.

A common approach to obtain the thermoelectric transport coefficients based on the DFT plus BoltzTraP calculation is to use a constant \(\tau\). It is obtained either from fitting of the experiments, or from the theoretical estimation. Here, thanks to the Q1D electronic structure, we go beyond this approach by taking into account the \(k\) dependence of \(\tau(k)\), contributed by the electron-phonon scattering. This makes our approach different from the common BoltzTrap calculation, and more closer to the real situation.
FIG. 2. DFT plus BoltzTraP calculation and model fitting. (a) The Fermi level ($E_f$) as a function of electron (red) and hole (black) doping at $T = 300$ K. The weak dependence of the $E_f$ on doping across three decades is characteristic of quasi-one-dimensional energy band. (b)-(c) The dependence of $\kappa_e/\tau$ and $S^2\sigma/\tau$ on $E_f$. The points are results from DFT plus BoltzTrap calculation, while the lines are from the 1D tight-binding model with the hopping parameter $t$ fitted from the band structure in Fig. 1 (b).

C. Phonon transport.

To get $ZT$, we also need the phonon thermal conductivity $\kappa_{ph}$, which we calculated by MD simulation. The following results are obtained from a simulation cell of $4 \times 6 \times 4$ unit cells in $x$, $y$, and $z$ directions, respectively, to overcome the finite size effect (SI Sec. S2). As shown in Fig. 4, the thermal conductivity of BDTMC shows a very weak temperature dependence over the temperature range considered (100-350 K). We get a value of $0.34 \pm 0.02$ W/m-K at 300 K. This weak temperature dependence is normally observed at high temperature limit, well within the validity of classical MD simulation.

The low thermal conductivity originates from the weak intermolecular bonding of Van der Waals (VDW) nature, in contrast to the strong intramolecular valence bonding. Different kinds of bonds result in very different frequency/time scales of inter- and intra-molecular dynamics. The thermal conductivity of the molecular crystal is dominated by the low-frequency inter-molecular vibrations. Their frequency mismatch with the intramolecular vibrations prevents efficient heat transport between molecules, good for thermoelectric performance. That is, most of the energy is localized inside each molecule, instead of transferred to other molecules. This can be seen from the large overshoot of $\kappa_{ph}$ as a function correlation time in Fig. S3.

D. Thermoelectric performance.

We are now in the position of evaluating the thermoelectric figure of merit $ZT$ defined in the beginning. It is shown in Fig 3(d). We get an optimal room-temperature

We use the 1D model parameter $t$ from fitting to the DFT electronic structure, and the Bardeen-Schockley deformation potential theory to take into account the electron-phonon scattering (SI Sec. S1). The relevant transport coefficients $\kappa_e$, $\sigma$ are shown in Fig. 3(a) and (b). We see a better transport performance of the holes. It can be attributed to their larger hopping amplitude $t$, leading to larger group velocity. Moreover, a strong deviation of the Wiedemann-Franz law is observed in Fig. 3(c), typical at the band edges or low dimensional structures. The smaller value of $\kappa_e/(T\sigma) < L$ indicates reduced electron thermal conductivity, and good thermoelectric performance.
FIG. 3. Thermoelectric transport coefficients at 300 K. (a)-(b) The electron thermal conductivity $\kappa_e$ and electrical conductivity $\sigma$ as a function of electron (n) and hole (p) doping. (c) $\kappa_e/\sigma$-$T$ as a function of doping, in unit of the Lorentz number $L = \pi^2k_B^2/(3e^2)$, such that the Wiedemann-Franz law corresponds to $\kappa_e/\sigma$-$T = L$. (d) $ZT$ as a function of doping.

$ZT$ of 0.38 at electron doping of $\sim 3.2 \times 10^{20} \text{ cm}^{-3}$, and 1.48 at hole doping of $\sim 1.57 \times 10^{20} \text{ cm}^{-3}$. The corresponding Seebeck coefficients are $-199 \mu\text{V/K}$ for electrons and $266 \mu\text{V/K}$ for holes. The electron and hole mobility at optimal doping are $\sim 2.4$ and $\sim 12.8 \text{ cm}^2/\text{V-s}$, respectively. These results are summarized in Table I. Finally, in Fig. 5, we plot the temperature dependence of the $ZT$. It shows an approximately linear dependence on $T$. The $ZT$ value is promising over a wide temperature range (100-350 K).

The Q1D electrical transport and low phonon thermal conductivity we obtained here originate from the chemical nature of the inter-molecular bonding. In our calculation, the conduction and valence band structures of BDTMC are determined by only one parameter, $t$, reflecting the strength of the $\pi$-$\pi$ VDW bonding. By comparing results of the CB and VB, we deduce that stronger bonding, thus larger $t$, results in better thermoelectric performance. Due to this simple, yet reasonably accurate model, we expect the results are quite general, and applicable to other $\pi$-$\pi$ stacking molecular crystals.

Although we only take into account the electron-phonon scattering in our calculation, the electron mobility obtained is in reasonable agreement with recent experimental results of these materials $^{21,24,25}$, and so are the Seebeck coefficients$^{30}$. All these put our prediction on a solid ground waiting for possible experimental confirmation.

III. CONCLUSIONS

In summary, we have studied the electronic structure of the BDT molecular crystal using the first-principles calculations. Based on the band structure, we find that the thermoelectric transport along the $\pi$-$\pi$ stacking direction is quasi-one-dimensional (Q1D). This is evident from its band dispersion and the density of states, proved by fitting the DFT results with a 1D tight-binding model. We then calculated the thermoelectric transport properties along $y$ direction using our 1D model. Furthermore, our classical molecular dynamics calculation gives a low phonon thermal conductivity. This is due to the weak VDW nature of the binding force between different...
TABLE I. Summary of important parameters and results for the conduction (CB) and valence band (VB): \( t \) the hopping parameter in the 1D model, \( m^* \) effective mass, \( D \) deformation potential, \( \mu \) mobility at optimal doping, \( S \) Seebeck coefficient at optimal doping (\( n \)).

|       | \( t \) (eV) | \( m^* \) (\( m_0 \)) | \( D \) (eV\(^2\)) | \( n \) (10\(^{20}\) cm\(^{-3}\)) | ZT | \( \mu \) (cm\(^2\)/V-s) | S (\( \mu \)V/K) | \( \kappa_e \) (W/m-K) |
|-------|-------------|-----------------------|---------------------|--------------------------|----|------------------|----------------|------------------|
| CB    | 0.05 (0.08) | 4.27                  | 6.67                | 3.19                      | 0.38 | 2.4          | -199         | 0.06             |
| VB    | 0.2         | -1.5                  | 8.55                | 1.57                      | 1.48 | 12.8         | 266          | 0.15             |

FIG. 4. Phonon thermal conductivity. The phonon thermal conductivity as a function of temperature obtained from the classical molecular dynamics simulation.

FIG. 5. Temperature dependence of \( ZT \) at optimal doping.

molecules. Thus, the BDTMC is a “phonon-glass”. Both Q1D electronic transport and phonon-glass-like thermal transport are prerequisite for highly efficient thermoelectric materials. Our results suggest that they can be realized at the same time in BDTMC, a direct consequence of \( \pi-\pi \) stacking. Our results, together with recent development in chemical control of the stacking angle and distance\(^{21,22} \), point out possible way of further enhancing the thermoelectric performance by chemical or mechanical engineering of \( \pi-\pi \) overlap integral.

IV. METHODS

A. DFT calculation.

The electronic structure is calculated using VASP, which uses plane wave basis set, and PAW pseudopotentials\(^{26} \). The Perdew-Burke-Ernzerhof (PBE) version of generalized gradient approximation (GGA) is used for the exchange-correlation potential\(^{31} \). The DFT-D2 method of Grimme is used to take into account the VDW interaction between different molecules\(^{32} \). The cutoff energy of the plane wave expansion is set to 400 eV. For the geometry optimization, the reciprocal space is sampled by a 4\( \times \)4\( \times \)4 Monkhorst-Pack \( k \)-meshes. The convergence criteria for the DFT self-consistent loop is set as 10\(^{-4} \) eV. In the band structure and DOS calculation, a finer mesh of 8\( \times \)8\( \times \)8 is used. We note that GGA without VDW or LDA calculation gives slightly different unit cells. But the final results are not sensitive to these small changes. Thus, we only show results from GGA plus VDW calculation.

The electronic structure contribution to the thermoelectric transport properties are calculated using the BoltzTraP code\(^{27} \). It is based on the semi-classical Boltzmann transport theory in the constant relaxation time approximation. The DFT result is fitted using a 1D tight-binding model. Based on their excellent agreement, further calculations are performed using the 1D model. Details of the 1D model are given in the SI.

B. MD simulation.

Equilibrium molecular dynamics (EMD) based on the Green-Kubo method is performed to get the thermal conductivity. The simulations were carried out using LAMMPS\(^{33} \). The periodic boundary condition is applied to a large enough super-cell (4\( \times \)6\( \times \)4 MD unit cells) in all three directions to avoid possible finite size effect. The
potential functions and parameters are based on Ref. 26. Details of the methods can be found in the SI.

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1 G. J. Snyder and E. S. Toberer, Nat. Mater. 7, 105 (2008).
2 G. Chen, M. S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial, and T. Caillat, Int. Mater. Rev. 48, 45 (2003).
3 M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J. P. Fleurial, and P. Gogna, Adv. Mater. 19, 1043 (2007).
4 Y. Dubi and M. DiVentra, Rev. Mod. Phys. 83, 131 (2011).
5 L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993).
6 L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 16631 (1993).
7 A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, Nature 451, 163 (2008).
8 A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J. Yu, W. A. Goddard III, and J. R. Heath, Nature 451, 168 (2008).
9 T. Markussen, A. Jauho, and M. Brandbyge, Phys. Rev. Lett. 103, 055502 (2009).
10 N. Li, J. Ren, L. Wang, G. Zhang, P. Hänggi, and B. Li, Rev. Mod. Phys. 84, 1045 (2012).
11 L.-D. Zhao, V. P. Dravid, and M. G. Kanatzidis, Energy Environ. Sci. 7, 251 (2014).
12 K. Koumoto, Y. Wang, R. Zhang, A. Kosuga, and R. Funahashi, Annu. Rev. Mater. Res. 40, 363 (2010).
13 L. Yang, N. Yang, and B. Li, Nano Lett. 14, 1734 (2014).
14 L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uber, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, Nature 508, 373 (2014).
15 Q. Zhang, Y. Sun, W. Xu, and D. Zhu, Adv. Mater. 26, 6829 (2014).
16 A. I. Casian and I. I. Sanduleac, J. Thermoelectricity 3 (2013).
17 N. Mateeva, H. Niculescu, J. Schlenoff, and L. R. Testardi, J. Appl. Phys. 83, 3111 (1998).
18 M. Pfeiffer, A. Beyer, T. Fritz, and K. Leo, Appl. Phys. Lett. 73, 3202 (1998).
19 R. Yue and J. Xu, Synthetic Metals 162, 912 (2012).
20 G.-H. Kim, L. Shao, K. Zhang, and K. P. Pipe, Nat. Mater. 12, 719 (2013).
21 H. Dong, X. Fu, J. Liu, Z. Wang, and W. Hu, Adv. Mater. 25, 6158 (2013).
22 G. Giri, E. Verploegen, S. C. B. Mannsfeld, S. Atahan-Evrenk, D. H. Kim, S. Y. Lee, H. A. Becerril, A. Aspuru-Guzik, M. F. Toney, and Z. Bao, Nature 480, 504 (2011).
23 D. Wang, W. Shi, J. Chen, J. Xi, and Z. Shuai, Phys. Chem. Chem. Phys. 14, 16505 (2012).
24 L. Zhang, L. Tan, W. Hu, and Z. Wang, J. Mater. Chem. 19, 8216 (2009).
25 L. Zhang, L. Tan, Z. Wang, W. Hu, and D. Zhu, Chem. Mater. 21, 1993 (2009).
26 G. Kresse and J. Furthmiller, Comp. Mater. Sci. 6, 15 (1996).
27 G. K. H. Madsen and D. J. Singh, Comput. Phys. Commun. 175, 67 (2006).
28 J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).
29 F. B. Beleznay, F. Bogr, and J. Ladik, J. Chem. Phys. 119, 5090 (2003).
30 X. Jiang, Z. Wei, and X. Qiu, Private communications.
31 J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
32 S. Grimme, J. Comput. Chem. 25, 1463 (2004).
33 S. Plimptone, J. Comp. Phys. 117, 1 (1995).