<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Journal of Chemical Physics*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Mirsakiyeva, A., Hugosson, H W., Linares, M., Delin, A. (2017)
Temperature dependence of band gaps and conformational disorder in PEDOT and its selenium and tellurium derivatives: density functional calculations.
Journal of Chemical Physics

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-214934>

Temperature dependence of band gaps and conformational disorder in PEDOT and its selenium and tellurium derivatives: density functional calculations

Amina Mirsakiyeva,^{1, a)} Håkan W. Hugosson,² Mathieu Linares,^{3, 4} and Anna Delin^{1, 4, 5, b)}

¹⁾ *Department of Applied Physics, School of Engineering Sciences, KTH Royal Institute of Technology, Electrum 229, SE-16440 Kista, Sweden*

²⁾ *Department of Electronics, Mathematics and Natural Sciences, University of Gävle, SE-80176 Gävle, Sweden*

³⁾ *Department Theoretical Chemistry and Biology, School of biotechnology, KTH Royal Institute of Technology, SE-10691 Stockholm, Sweden*

⁴⁾ *Swedish e-Science Research Center (SeRC), KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden*

⁵⁾ *Department of Physics and Astronomy, Materials Theory Division, Uppsala University, Box 516, SE-75120 Uppsala, Sweden*

(Dated: 8 September 2017)

The conducting polymer poly(3,4-ethylenedioxythiophene), or PEDOT, is an attractive material for flexible electronics. We present combined molecular dynamics and quantum chemical calculations, based on density functional theory, of EDOT oligomers and isoelectronic selenium and tellurium derivatives (EDOS and EDOTe) to address the effect of temperature on the geometrical and electronic properties of these systems. With finite size scaling, we also extrapolate our results to the infinite polymers, i.e. PEDOT, PEDOS and PEDOTe. Our computations indicate that the most favourable oligomer conformations at finite temperature are conformations around the flat trans-conformation and a non-flat conformation around 45° from the cis-conformation. Also, the dihedral stiffness increases with the atomic number of the heteroatom. We find excellent agreement with experimentally measured gaps for PEDOT and PEDOS. For PEDOT, the gap does not increase with temperature whereas this is the case for its derivatives. The conformational disorder as well as the choice of basis set both significantly affect the calculated gaps.

PACS numbers: Valid PACS appear here

Keywords: PEDOT, selenium, tellurium, density functional theory, Car-Parrinello molecular dynamics

I. INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the experimentally most well-studied conjugated polymers. This material combines a number of very attractive properties such as optical transparency in the conducting state, high stability in air and at elevated temperatures, and high processability¹. PEDOT was initially developed by Bayer AG in the late 1980s for use as an antistatic agent and as electrode material². Today, PEDOT is a widely used material in many commercial applications such as, e.g., touch screens for mobile phones and flat panel displays, electronic paper, and solar cells.

The PEDOT polymer consists of chains of EDOT units, see Figure 1. Each EDOT pair is connected via a C-C bond (the one connecting atoms 4 and 5 in Figure 1c). In the ground state, the polymer has an aromatic character (Figure 1a) and the bond connecting two consecutive EDOT is a single bond (1.54 Å). In the excited state, the polymer adopts a quinoid-like character (Figure 1b) and the bond connecting two consecutive EDOT

is double (1.34 Å). The most stable conformation has adjacent EDOT monomers ordered in the trans-position, see Figure 1c, forming a flat structure (the dihedral angle 7-4-5-8 is close to 0°). The EDOT units rotate easily around the bond connecting adjacent units. For the polymer, this results in a large number of conformational degrees of freedom and, at finite temperature, high torsional disorder. In the gas phase, the dihedral angle rotations require energies of typically around or less than 1 meV per degree and inter-ring bond³, and are therefore easily activated by thermal fluctuations at ambient temperature ($k_B T = 25.7$ meV at $T = 298$ K, where k_B denotes the Boltzmann constant).

In general, substituting specific atoms or functional groups in conducting polymers is a viable strategy for developing new materials for organic electronics. With such substitution, it is possible to tune many fundamental properties, e.g., the polarizability, dielectric constant, intermolecular interactions or the optical absorption spectrum. PEDOS is a derivative of PEDOT, in which the heteroatom sulfur atoms have been replaced by isoelectronic selenium. This material has a smaller energy gap compared to PEDOT. It also has excellent electrochromic properties⁴⁻⁶. Further isoelectronic substitution of sulfur with even heavier atoms than selenium is conceivable. Due to the large spin-orbit coupling in elements with

^{a)} Electronic mail: aminami@kth.se

^{b)} Electronic mail: annadel@kth.se

FIG. 1. (a) Aromatic structure of PEDOT. (b) Quinoid structure of PEDOT. (c) Trans-positioning and (d) cis-positioning of adjacent EDOT monomers. In the cis-position, the dihedral angle is 0° , and in the trans-position, it is 180° . The numbered carbon atoms 1-6 in panel (c) constitute the carbon backbone. Atoms 7 and 8 are the heteroatoms.

high atomic number, such derivatives of PEDOT could become useful in spintronics applications for detecting spin currents through the inverse spin hall effect (ISHE)⁷. The next derivative in the isoelectronic series would be PEDOTe, where the sulfur atoms have been replaced by tellurium. This system, however, appears to be challenging to synthesize, although related tellurium-containing polymers have indeed been successfully synthesized⁸.

Detailed investigation of the consequences of conformational disorder in these systems are very scarce. In general, it can be expected that non-planarity and disorder will affect the fundamental properties of the polymers. For example, non-planarity reasonably causes a localization of the otherwise delocalized valence and conduction bands in conjugated polymers, resulting in a deterioration of the transport properties⁹. In particular, it has been demonstrated that dihedral angle rotations cause the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) to increase significantly in PEDOT and PEDOS^{10,11}, as well as in polythiophene and polyselenophene^{3,12}. This may be an important reason why it has proved difficult to construct devices with optimal charge carrier mobility based on these polymers.

Recently, Bombile and coworkers⁹ addressed the effect of dihedral disorder on the optoelectronic properties of polythiophenes using a tight-binding approach. They found that dihedral disorder indeed tends to shift the absorption peak toward higher frequencies.

Due to the significant computational cost, density functional theory (DFT) computations have hitherto mostly been employed to address highly ordered sys-

tems of conducting polymers^{13–17}. As soon as disorder is invoked, the computations become very demanding. With modern computational resources however, it is possible to address disorder directly at the DFT level. Here, we present detailed systematic calculations, using DFT-based molecular dynamics simulations, of how the structure of EDOT oligomers and its selenium and tellurium derivatives vary as a function of temperature and oligomer length, and how this variation affects the electronic structure properties of the oligomer. The computed data allow us to draw conclusions concerning aromatic/quinoid character, and to analyze how the conformation affect the HOMO–LUMO gaps. In a previous work, we have presented computations of the dihedral angle distributions for 12-oligomers of EDOT, EDOS, and EDOTe at 300 K.¹⁸

II. THEORY AND COMPUTATIONAL DETAILS

The ground-state structure optimization as well as the quantum molecular dynamical simulations were carried out using the Car-Parrinello molecular dynamics (CPMD) method^{19,20} with periodic boundary conditions in all three dimensions. The detailed setup used is very similar to the one used in a previous paper,¹⁸ but for clarity, we repeat the pertinent details here. The CPMD method treats all atoms of the system quantum mechanically at the density functional theory (DFT) level. The interatomic forces are calculated at each time step, keeping the electron orbital functions close to the Born-Oppenheimer surface with the help of fictitious dynamics. In the present calculations, we used a fictitious electron mass of 800 atomic units and a time step of $\Delta t = 0.1$ fs to integrate the equations of motion. We employed the BLYP^{21,22} approximation for the exchange-correlation part of the total energy functional. The effect of the core electrons was described using Troullier-Martins norm-conserving pseudopotentials²³ and the valence electron wave functions were expanded in a plane-wave basis set with a kinetic cut-off of 90 Ry.

To simulate the neutral oligomers, an orthorhombic simulation box containing one oligomer was used. The size of the simulation box was chosen large enough to avoid oligomer-oligomer interaction. Thus, the simulation box along the oligomer chain was scaled so that the vacuum distance between adjacent polymers and walls of the box along the x , y - and z -directions was set to 4 Å, i.e. the molecule-molecule distance was at least 8 Å in all directions. With this box size, the orbital overlap between adjacent oligomers was found to be negligible²⁴.

The initial configuration was chosen to be planar, with atomic distances taken from Kim and Brédas.²⁵ From this initial guess, the ground-state structure was found through quenching and annealing for 2.5 ps. The system was subsequently equilibrated during 5 ps. In this step, the temperature was controlled by rescaling the velocities so as to keep the system within a 40 K toler-

ance window around the target temperature. We selected 200 K, 300 K and 400 K as target temperatures to investigate the effect of temperature on the oligomer properties. After equilibration followed a MD run of 50 ps for each target temperature, during which statistics were collected. Here, temperature control was implemented for both the atomic and electronic degrees of freedom using Nosé-Hoover thermostats^{26,27} with a characteristic frequency of 10000 cm^{-1} for the electrons and 480 cm^{-1} for the atoms.

The HOMO-LUMO gaps were calculated as a function of twisting angle for oligomers of EDOT, EDOS and EDOTe at the B3LYP^{22,28–30} level using the Gaussian 09 software package.³¹ In these computations, we employed both the 6-31+G(d) and the LanL2DZ basis sets. To find the HOMO-LUMO gap of the infinitely long polymer, we performed finite size scaling using our computed data for the dimers, tetramers and hexamers. As it is well known, linear regression gives incorrect results³² and more elaborate schemes must be used. Specifically, we fitted our data to the equation

$$E = E_0 \sqrt{1 + 2 \frac{k'}{k_0} \cos \frac{\pi}{N+1}}. \quad (1)$$

This finite size scaling approach is based on a simple model of the polymer as a chain of identical oscillators, and was first used by W. Kuhn³³ to address polyene. Here, E is the gap and N is the number of double bonds along the shortest path connecting the terminal carbon atoms of the molecular backbone. E_0 and k'/k_0 are treated as free parameters in the fit. In the model, E_0 corresponds to the vibration energy of a single oscillator, k_0 is the force constant of the isolated oscillator, and k' is the force constant coupling two adjacent double bonds. Finally, the effect of conformational disorder on the gap size was modeled by performing a weighted average of the computed gap with respect to the dihedral angle distribution.

III. RESULTS AND DISCUSSION

In the ground state, i.e. at 0 K, adjacent monomers are in the trans-position and the polymer is flat with the dihedral angles close to 180° . We find that the heteroatom orbitals substantially contribute to the LUMO in all cases. In contrast, the HOMO typically shows very little weight at the heteroatom positions, see Figures S1–S8 in Supplementary Material. As regards structural parameters of the monomers and oligomers in the ground state, see Figure S9 in Supplementary Material. Our results are very similar to previous work for EDOT, EDOS and their oligomers.^{12,25,34,35}

The molecular dynamics simulations allow us to explicitly study the effect of finite temperature on the structural and electronic properties of the oligomer. Since the energies associated with dihedral rotations are small,

TABLE I. Planarity factor for hexamers of PEDOT, PEDOS and PEDOTe at 200 K, 300 K and 400 K. The numbers in parentheses refer to the one standard deviation widths of the distributions.

Oligomer	$T=200\text{ K}$	$T=300\text{ K}$	$T=400\text{ K}$
6EDOT	0.67 (0.11)	0.64 (0.08)	0.67 (0.08)
6EDOS	0.71 (0.14)	0.64 (0.10)	0.60 (0.13)
6EDOTe	0.78 (0.11)	0.66 (0.08)	0.57 (0.14)

dihedral angle distributions can be expected to vary sensitively with temperature. Figure 2 shows the dihedral angle distributions around the trans-position (180°) for hexamers of EDOT, EDOS and EDOTe at three different temperatures. For 6EDOT (hexamer of EDOT), the distribution seems to be relatively independent of the temperature in the range studied, whereas for 6EDOS and 6EDOTe (hexamers of EDOS and EDOTe, respectively), as temperature increases, the distributions broaden significantly and the total population diminishes in this range of dihedral angles. For shorter oligomers, (tetramers and dimers), the distributions widen for all three studied systems, although the trend is weaker for the EDOT oligomers compare to the EDOS and EDOTe oligomers, (see Supplementary Material, Figures S10 and S11). The trends in the dihedral distributions agree with the observed higher stiffness of oligomers the heavier the heteroatom is. At 200 K, the distribution for 6EDOT is already quite broad, whereas a higher temperature is needed for 6EDOS and 6EDOTe to reach a similar broadness. This is illustrated in Figure 3, where we show the change in total energy for the dimers as a function of dihedral angle. Our motivation for choosing the LanL2DZ basis set is shown in the Supplementary Material section, Figures S12 and S13.

All oligomers show a second peak in the dihedral angle distribution around 45° away from the cis-position. These peaks are displayed in Figure 4 for hexamers of EDOT, EDOS and EDOTe as a function of temperature. They appear due to the competition between steric hindrance (favouring a non-flat oligomer configuration) and π -conjugation (favouring a flat oligomer configuration)³⁶. In the Supplementary Material we discuss this issue further and also compare with polythiophene (Figure S14).

For 6EDOT, the population in this range of angles appears to be independent of temperature. For the selenium and tellurium derivatives, the population increases with temperature. The observed trends match those observed around the trans-position visible in Figure 2. To summarize the statistics gathered from the dihedral angle distribution in a single number, we computed a planarity measure P as recently introduced by Sjöqvist et al.³⁷, see Table 1. P is zero when adjacent monomers are in either the trans- or cis-position, and 1 when adjacent monomers are perpendicular to each other. The planarity of the oligomer is calculated as the average of

FIG. 2. (Color online) Dihedral angle distributions around the trans-position conformation for 6EDOT (black lines in panels a, b, c), 6EDOS (red lines in panels d, e, f), and 6EDOTe (blue lines in panels g, h, i) hexamers at 200 K (left-most column, i.e. panels a, d, g), 300 K (middle column, i.e. panels b, e, h) and 400 K (right-most column, i.e. panels c, f, i) from 90° to 270° .

FIG. 3. Total energy versus twisting angle 2EDOT, 2EDOS and 2EDOTe, using the B3LYP approximation to the exchange-correlation functional and the LanL2DZ gaussian basis set.

the deviation from the perpendicular conformation, i.e.

$$P = \left\langle \frac{1}{n} \sum_i^n \frac{|\theta_i - 90|}{90} \right\rangle, \quad (2)$$

where the dihedral angle θ_i is given in degrees and n is the number of inter-monomer bonds. Thus, for each time step we calculated the average planarity of the oligomer, obtaining a normalized value in the range 0 to 1. Finally, we averaged over the whole MD trajectory of 50 ps,

as indicated by the brackets $\langle \dots \rangle$ in Eq. 2. Apparently, the planarity for 6EDOT is essentially unchanged in the studied temperature range, whereas it decreases with temperature for both the selenium and tellurium derivatives. The decrease is especially large for 6EDOTe. At 200 K, 6EDOTe is the most planar of the three hexamers ($P = 0.78$), whereas at 400 K, it is the most non-planar ($P = 0.57$).

Closely connected to the dihedral angle distributions and the planarity, is the inter-monomer distance d_{X-O} , between heteroatom X, where X stands for S, Se, and Te, and the closest oxygen atom on each adjacent monomer. For planar oligomers in the trans-position, this distance should attain its smallest possible value. In Table II, d_{X-O} is tabulated for all studied oligomers and temperatures. For comparison, the values for completely flat oligomers are also given. The data in this table further supports the conclusions drawn from the planarity analysis above. For example, we see that d_{X-O} in most cases tend to increase with temperature.

Our analysis of the bond lengths along the polymer backbone for the hexamers show no clear correlation with either temperature in the range 200 K–400 K, or with heteroatom type. However, at 0 K, the bond variations are clearly larger at the edges of the oligomers compared to the center, see Figure S9 in Supplementary Material. All oligomers were found to prefer an aromatic-like state. Additional results for the carbon backbone can be found

FIG. 4. (Color online) Dihedral angle distributions around the trans-position conformation for 6EDOT (black lines in panels a, b, c), 6EDOS (red lines in panels d, e, f), and 6EDOTe (blue lines in panels g, h, i) hexamers at 200 K (left-most column, i.e. panels a, d, g), 300 K (middle column, i.e. panels b, e, h) and 400 K (right-most column, i.e. panels c, f, i) from 0° to 90° , showing the dihedral angle distributions centered 45° away from the cis-position conformation.

TABLE II. Average inter-monomer heteroatom-oxygen distances d_{X-O} , expressed in ångström. The numbers in parentheses refer to the one standard deviation widths of the distributions.

Oligomer	$T=0$ K (flat)	$T=200$ K	$T=300$ K	$T=400$ K
2EDOT	2.96	3.1 (0.003)	3.0 (0.003)	3.5 (0.004)
4EDOT	2.95	3.1 (0.02)	3.2 (0.22)	3.1 (0.22)
6EDOT	2.92	3.6 (0.42)	3.5 (0.42)	3.5 (0.64)
2EDOS	2.95	3.0 (0.001)	3.0 (0.002)	3.1 (0.01)
4EDOS	2.94	3.0 (0.01)	3.1 (0.02)	3.3 (0.28)
6EDOS	2.94	3.1 (0.29)	3.6 (0.42)	3.8 (0.22)
2EDOTe	2.94	3.0 (0.003)	3.0 (0.0002)	3.0 (0.003)
4EDOTe	2.93	3.0 (0.008)	3.0 (0.008)	3.1 (0.1)
6EDOTe	2.93	3.3 (0.27)	3.6 (0.42)	4.0 (0.38)

in the Supplementary Material, Figure S9.

The size of the band gap is a key parameter for many technological applications. In oligomers, the band gap depends on, e.g., the oligomer length and the conformation. The experimentally measured gap may also depend on, e.g., whether the polymer is in film form or in solution, the polarity of the solvent used, and the degree of residual doping of the polymer. For PEDOT and derivatives thereof, absorption spectroscopy indicates that the difference in the gap is less than 0.1 eV between PEDOT in solution and PEDOT in film form.^{38,40} The

computed band gap also depends quite sensitively on the computational approach used. Especially the discontinuity in the exchange-correlation functional is often pointed out as the main source of error. Earlier calculations of the HOMO-LUMO gap in PEDOT using DFT-based methods report values ranging from 0.7 eV to 2.7 eV. The large variation in the reported results can be attributed to differences in choice of functional, finite size scaling method used (or absence thereof), and geometrical details.^{4,17,34,35,41,42} In these earlier studies, larger gaps were found for shorter oligomers compared to longer oligomers⁴¹. Also, the generalized gradient correction was found to give small gaps¹⁷ whereas the B3LYP functional was found to give larger gaps⁴¹ in closer agreement with experiment.

For PEDOS, a computed HOMO-LUMO gap of 1.66 eV has been reported.³⁵ In all these previous calculations, the B3LYP functional tends to give the most reasonable values for the HOMO-LUMO gap.

In the left-most column in Figure 5 (a, c, and e) we show the HOMO-LUMO gaps computed with the B3LYP functional combined with two different basis sets: 6-31+G(d) and LanL2DZ. The amount of exchange in the B3LYP functional is empirically optimized to reproduce the experimental gaps in a range of small molecules. Thus, any additional major errors in calculated gaps can be expected to originate from other sources. In Figure 5,

FIG. 5. (Color online) For hexamers (dashed lines) and extrapolated polymers (straight lines) of PEDOT (a and b), PEDOS (c and d) and PEDOTe (e and f) using B3LYP together with 6-31+G(d) (black lines) and LanL2DZ (red lines). Left column (a, c and e) is presenting gaussian calculations of HOMO-LUMO energy gap [eV] vs twisting angle [°]; right column (b, d and f) shows weighted averages of the HOMO-LUMO gaps [eV] over 50 fs of CPMD calculations vs T [K] and experimental data: black triangle right - UV-Visible spectroscopy of PEDOT at room temperature³⁸, black triangle left - optical absorption of electro-oxidized PEDOT at room temperature³⁹, black circle - spectroelectrochemistry of PEDOS film⁴

all dashed lines refer to results for hexamers, whereas the full lines refer to the value of the gap in the corresponding infinite polymer, calculated with finite size scaling³² as described earlier. For all three studied hexamers, we see that the gap varies significantly with the dihedral angle. As expected, the largest gaps are found around a dihe-

dral angle of 90°, where the π -conjugation is minimal. In our computations we model the dihedral rotation with an equidistant spiral twisting of the oligomers.

Also, the gap for PEDOTe is significantly smaller than that of PEDOT and PEDOS. This reflects the much more extended valence orbitals of the tellurium ion, and its

more metallic character, compared to sulphur and selenium.

Our computations of the dihedral angle distributions allow us to address how the average HOMO-LUMO gap in these systems changes with temperature. The right-most column in Figure 5 (b, d, and f) shows the HOMO-LUMO gap for each case weighted with the corresponding dihedral angle distribution. Five interesting results can be identified. First, we find that the average gap in 6EDOT/PEDOT is essentially constant in the studied temperature range, whereas the gap increases significantly for both 6EDOS/PEDOS and 6EDOTe/PEDOTe with temperature so that at 400 K it is around 0.2-0.4 eV higher than at 200 K. Second, we find that the size of the gap increases with around 0.3 eV at 300 K for 6EDOT/PEDOT and 6EDOS/PEDOS due to the conformational disorder (for 6EDOTe/PEDOTe the trend is unclear) compared to the 0 K results. Third, we find that the choice of basis set (6-31+G(d) versus LanL2DZ) has a significant impact on the gap. The 6-31+G(d) basis gives between 0.2 and 0.5 eV larger gaps. Fourth, finite size scaling lowers the gaps with typically 0.3-0.4 eV. Thus, all these issues significantly affect the computed band gaps and to make a fair comparison with experiment, all of them need to be addressed. Finally, with the 6-31+G(d) basis set, we find excellent agreement between the experimentally measured gap (the black triangles in Figure 5b) and our computed gap for PEDOT (full black line). The same is true for PEDOS if we use the LanL2DZ basis set. Here, the experimental value is the black filled circle in Figure 5d, and the computed gap is given by the full red line.

IV. CONCLUSIONS

In conclusion, we have used a combination of CPMD simulations, quantum chemical computations using the Gaussian software package, and finite size scaling to address finite temperature properties of PEDOT and its isoelectronic derivatives PEDOS and PEDOTe. In all cases, we address isolated chains in the gas phase. We find that the HOMO-LUMO gap depends significantly on temperature for PEDOS and PEDOTe, whereas this is not the case for PEDOT. However, the conformational disorder is important to take into account in all three cases. We also find that the choice of basis set affects the gap quite significantly. With all corrections taken into account, we find excellent agreement with experimentally measured gaps for PEDOT and PEDOS if we use the 6-31+G(d) basis set for PEDOT and the LanL2DZ basis set for PEDOS. Our computations also indicate that the dihedral stiffness of these systems increases with the heteroatom and that the most common oligomer conformations at finite temperature are the flat trans-conformation and a non-flat conformation around 45° from the cis-conformation. Temperature fluctuations cause quite large deviations from these two main confor-

mations.

The electronic structure and the conformational disorder of the here studied polymers may conceivably also be affected by, e.g., solvents, dopants and interchain interactions. For example, dopants may affect the HOMO-LUMO gap with as much as 0.3 eV.¹⁷ All these issues are relevant to investigate but left for a future study.

SUPPLEMENTARY MATERIAL

See Supplementary Material for the next figures:

Figure S1-S4 - Highest occupied and lowest unoccupied for 6EDOT oligomer calculated with 2 different basis sets: 6-31G(d) and LanL2DZ.

Figure S5-S8 - Highest occupied and lowest unoccupied for 6EDOS and 6EDOTe oligomers calculated with LanL2DZ basis set. Those figures are showing influence of heteroatom on molecular orbitals.

Figure S9 - The bond lengths for C-C/C=C bonds of 6EDOT, 6EDOS and 6EDOTe at 200 K, 300 K and 400 K.

Figure S10 - Dihedral angle distributions of the 2EDOT, 2EDOS, and 2EDOTe dimers at 200 K, 300 K and 400 K from 90° to 270°, showing the dihedral angle distributions centered around the trans-position conformation.

Figure S11 - Dihedral angle distributions of the 4EDOT, 4EDOS, and 4EDOTe dimers at 200 K, 300 K and 400 K from 90° to 270°, showing the dihedral angle distributions centered around the trans-position conformation.

Figure S12 - Comparison of Gaussian calculations of HOMO-LUMO energy gap [eV] vs twisting angle [°] for 6EDOT under B3LYP for 6-31+G(d) and LanL2DZ basis sets.

Figure S13 - Comparison of Gaussian calculations of minimum energy [eV] vs twisting angle [°] for 2EDOT and 2EDOS under B3LYP for 6-31+G(d) and LanL2DZ basis sets.

Figure S14 - Comparison of Gaussian calculations of minimum energy[eV] vs twisting angle [°] for dimers of PEDOT (2EDOT here) and polithiophene (2T here) under B3LYP with 6-31+G(d) basis set.

Figure S15 - Comparison of Gaussian calculations of minimum energy [eV] vs twisting angle [°] for dimers of PEDOT (2EDOT here) under B3LYP (black line) and BLYP (red line) with LanL2DZ basis set and BLYP (blue line) with planewave basis set.

ACKNOWLEDGEMENTS

We grateful to Dr. Lars Bergqvist for the valuable scientific discussions. We also acknowledge financial support from Vetenskapsrådet (VR), The Royal Swedish Academy of Sciences (KVA), the Knut and Alice Wallenberg Foundation (KAW), Carl Tryggers Stiftelse (CTS),

Swedish Energy Agency (STEM), and Swedish Foundation for Strategic Research (SSF). The computations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Center (NSC), Linköping University, the PDC Centre for High Performance Computing (PDC-HPC), KTH, and the High Performance Computing Center North (HPC2N), Umeå University.

- ¹S. Kirchmeyer and K. Reuter, "Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene)," *J. Mater. Chem.* **15**, 2077–2088 (2005).
- ²F. Jonas, G. Heywang, W. Schmidtberg, J. Heinze, and M. Dietrich, "Neue polythiophene, verfahren zu ihrer herstellung und ihre verwendung," (1989), eP Patent App. EP19,890,106,236.
- ³S. S. Zade and M. Bendikov, "Twisting of conjugated oligomers and polymers: Case study of oligo- and polythiophene," *Chem. Eur. J.* **13**, 3688–3700 (2007).
- ⁴A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitius, and M. Bendikov, "Poly(3,4-ethylenedioxy-selenophene)," *J. Am. Chem. Soc.* **130**, 6734–6736 (2008), <http://dx.doi.org/10.1021/ja8018675>.
- ⁵M. Li, A. Patra, Y. Sheynin, and M. Bendikov, "Hexyl-derivatized poly(3,4-ethylenedioxy-selenophene): Novel highly stable organic electrochromic material with high contrast ratio, high coloration efficiency, and low-switching voltage," *Adv. Mater.* **21**, 1707–1711 (2009).
- ⁶M. Li, Y. Sheynin, A. Patra, and M. Bendikov, "Tuning the electrochromic properties of poly(alkyl-3,4-ethylenedioxy-selenophenes) having high contrast ratio and coloration efficiency," *Chem. Mater.* **21**, 2482–2488 (2009), <http://dx.doi.org/10.1021/cm9003596>.
- ⁷K. Ando, S. Watanabe, S. Mooser, E. Saitoh, and H. Sirringhaus, "Solution-processed organic spincharge converter," *Nat. Mater.* **12**, 622627 (2013).
- ⁸E. I. Carrera and D. S. Seferos, "Semiconducting polymers containing tellurium: Perspectives toward obtaining high-performance materials," *Macromolecules* **48**, 297–308 (2015), <http://dx.doi.org/10.1021/ma502307b>.
- ⁹J. H. Bombile, M. J. Janik, and S. T. Milner, "Tight binding model of conformational disorder effects on the optical absorption spectrum of polythiophenes," *Phys. Chem. Chem. Phys.* **18**, 12521–12533 (2016).
- ¹⁰Y. H. Wijsboom, A. Patra, S. S. Zade, Y. Sheynin, M. Li, L. J. W. Shimon, and M. Bendikov, "Controlling rigidity and planarity in conjugated polymers: Poly(3,4-ethylenedithioselenophene)," *Angew. Chem. Int. Ed.* **48**, 5443–5447 (2009).
- ¹¹Y. H. Wijsboom, Y. Sheynin, A. Patra, N. Zamoshchik, R. Vardimon, G. Leitius, and M. Bendikov, "Tuning of electronic properties and rigidity in pedot analogs," *J. Mater. Chem.* **21**, 1368–1372 (2011).
- ¹²S. S. Zade and M. Bendikov, "From oligomers to polymer: Convergence in the homo-lumo gaps of conjugated oligomers," *Org. Lett.* **8**, 5243–5246 (2006), <http://dx.doi.org/10.1021/ol062030y>.
- ¹³P. Vogl and D. K. Campbell, "First-principles calculations of the three-dimensional structure and intrinsic defects in *trans*-polyacetylene," *Phys. Rev. B* **41**, 12797–12817 (1990).
- ¹⁴G. Zheng, S. J. Clark, S. Brand, and R. A. Abram, "First-principles studies of the structural and electronic properties of poly- para -phenylene vinylene," *J. Phys. Condens. Matter* **16**, 8609 (2004).
- ¹⁵P. Gomes da Costa, R. G. Dandrea, and E. M. Conwell, "First-principles calculation of the three-dimensional band structure of poly(phenylene vinylene)," *Phys. Rev. B* **47**, 1800–1810 (1993).
- ¹⁶R. A. Street, J. E. Northrup, and A. Salleo, "Transport in polycrystalline polymer thin-film transistors," *Phys. Rev. B* **71**, 165202 (2005).
- ¹⁷A. Lenz, H. Kariis, A. Pohl, P. Persson, and L. Ojamae, "The electronic structure and reflectivity of pedot:pss from density functional theory," *Chem. Phys.* **384**, 44 – 51 (2011).
- ¹⁸A. Mirsakiyeva, H. W. Hugosson, X. Crispin, and A. Delin, "Quantum molecular dynamical calculations of pedot 12-oligomer and its selenium and tellurium derivatives," *J. Electron. Mater.* , 1–5 (2016).
- ¹⁹R. Car and M. Parrinello, "Unified approach for molecular dynamics and density-functional theory," *Phys. Rev. Lett.* **55**, 2471–2474 (1985).
- ²⁰J. Hutter, A. Alavi, T. Deutsch, M. Bernasconi, S. Goedecker, D. Marx, M. Tuckerman, and M. Parrinello, "Cpmd: Carparinello molecular dynamics, version 3.17.1; copyright ibm corp, copyright mpi fr festkrperforschung stuttgart." (2000-2017).
- ²¹A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Phys. Rev. A* **38**, 3098–3100 (1988).
- ²²C. Lee, W. Yang, and R. G. Parr, "Development of the colle-salvetti correlation-energy formula into a functional of the electron density," *Phys. Rev. B* **37**, 785–789 (1988).
- ²³N. Troullier and J. L. Martins, "Efficient pseudopotentials for plane-wave calculations," *Phys. Rev. B* **43**, 1993–2006 (1991).
- ²⁴J. Cornil, D. A. dos Santos, X. Crispin, R. Silbey, and J. L. Brdas, "Influence of interchain interactions on the absorption and luminescence of conjugated oligomers and polymers: A quantum-chemical characterization," *JACS* **120**, 1289–1299 (1998), <http://dx.doi.org/10.1021/ja973761j>.
- ²⁵E.-G. Kim and J.-L. Brédas, "Electronic evolution of poly(3,4-ethylenedioxythiophene) (pedot): From the isolated chain to the pristine and heavily doped crystals," *J. Am. Chem. Soc.* **130**, 16880–16889 (2008), <http://dx.doi.org/10.1021/ja806389b>.
- ²⁶S. Nose, "A molecular dynamics method for simulations in the canonical ensemble," *Mol. Phys.* **52**, 255–268 (1984), <http://dx.doi.org/10.1080/00268978400101201>.
- ²⁷W. G. Hoover, "Canonical dynamics: Equilibrium phase-space distributions," *Phys. Rev. A* **31**, 1695–1697 (1985).
- ²⁸A. D. Becke, "Density-functional thermochemistry. iii. the role of exact exchange," *J. Chem. Phys.* **98**, 5648–5652 (1993).
- ²⁹S. H. Vosko, L. Wilk, and M. Nusair, "Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis," *Can. J. Phys.* **58**, 1200–1211 (1980), <http://dx.doi.org/10.1139/p80-159>.
- ³⁰P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, "Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields," *J. Phys. Chem.* **98**, 11623–11627 (1994), <http://dx.doi.org/10.1021/j100096a001>.
- ³¹M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuse-ria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, J. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision D.01," Gaussian Inc. Wallingford CT 2009.
- ³²J. Gierschner, J. Cornil, and H.-J. Egelhaaf, "Optical bandgaps of π -conjugated organic materials at the polymer limit: Experiment and theory," *Adv. Mater.* **19**, 173–191 (2007).
- ³³W. Kuhn, "ber das absorptionsspektrum der polyene," *Helv. Chim. Acta* **31**, 1780–1799 (1948).

- ³⁴A. Shalabi, S. A. Aal, and M. Assem, "Pedotspcnbms polymer-fullerene {BHJ} solar cells: Quantum mechanical calculations of photovoltaic and photophysical properties," *Nano Energy* **1**, 608 – 623 (2012).
- ³⁵E. Poverenov, Y. Sheynin, N. Zamoshchik, A. Patra, G. Leitush, I. F. Perepichka, and M. Bendikov, "Flat conjugated polymers combining a relatively low homo energy level and band gap: polyselenophenes versus polythiophenes," *J. Mater. Chem.* **22**, 14645–14655 (2012).
- ³⁶J. Roncali, F. Garnier, R. Garreau, and M. Lemaire, "Reduction of the steric hindrance to conjugation in 3,4-disubstituted poly(thiophenes); cyclopenta[c]thiophene and thieno[c]thiophene as precursors of electrogenerated conducting polymers," *J. Chem. Soc., Chem. Commun.*, 1500–1502 (1987).
- ³⁷J. Sjöqvist, J. Maria, R. A. Simon, M. Linares, P. Norman, K. P. R. Nilsson, and M. Lindgren, "Toward a molecular understanding of the detection of amyloid proteins with flexible conjugated oligothiophenes," *J. Phys. Chem. A* **118**, 9820–9827 (2014), <http://dx.doi.org/10.1021/jp506797j>.
- ³⁸F. Tran-Van, S. Garreau, G. Louarn, G. Froyer, and C. Chevrot, "Fully undoped and soluble oligo(3,4-ethylenedioxythiophene)s: spectroscopic study and electrochemical characterization," *J. Mater. Chem.* **11**, 1378–1382 (2001).
- ³⁹Q. Pei, G. Zuccarello, M. Ahlskog, and O. Ingans, "Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue," *Polymer* **35**, 1347 – 1351 (1994).
- ⁴⁰W.-C. Chen, C.-L. Liu, C.-T. Yen, F.-C. Tsai, C. J. Tonzola, N. Olson, and S. A. Jenekhe, "Theoretical and experimental characterization of small band gap poly(3,4-ethylenedioxythiophene methine)s," *Macromolecules* **37**, 5959–5964 (2004), <http://dx.doi.org/10.1021/ma049557f>.
- ⁴¹C. Alemn, E. Armelin, J. I. Iribarren, F. Liesa, M. Laso, and J. Casanovas, "Structural and electronic properties of 3,4-ethylenedioxythiophene, 3,4-ethylenedisulfanylfurane and thiophene oligomers: A theoretical investigation," *Synthetic Met.* **149**, 151 – 156 (2005).
- ⁴²A. Dkhissi, D. Beljonne, R. Lazzaroni, F. Louwet, L. Groenendaal, and J. L. Brdas, "Density functional theory and hartreefock studies of the geometric and electronic structure of neutral and doped ethylenedioxythiophene (edot) oligomers," *Int. J. Quantum Chem.* **91**, 517–523 (2003).