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A comparative MD study of the local structure of polymer semiconductors P3HT and PBTTT

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A comparative MD study of the local structure of polymer semiconductors P3HT and PBTTT

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Dear Editor

Please find enclosed the revised version of our paper "A comparative MD study of the local structure of polymer semiconductors P3HT and PBTTT" (Manuscript ID CP-ART-06-2010-000785), which we are resubmitting to Physical Chemistry Chemical Physics.

We have responded to the 6 points made by the referee and have made associated modifications to the manuscript, as indicated below.

We have also included the requested table of contents graphic. A suitable table of contents entry is: "Molecular dynamics simulations show the structural properties that facilitate intra- and inter-chain charge transport in PBTTT compared with P3HT."

Concerning the various options for publication of colour figures, if our paper is selected for publication, we are happy for the submitted colour figures to be converted to greyscale for the print article.

We hope that you will now find the manuscript suitable for publication in Physical Chemistry Chemical Physics.

Yours sincerely

David Huang,
for the authors

Referee: 1

1) We agree with the referee that our discussion of previous computer simulation work of semiconducting polymers (P3HT in particular) in the submitted paper was insufficient. Therefore, we have removed the line "We are aware of only one small system study of P3HT in the solid phase" (line 35-36, page 2) of section 2 and instead expanded on our discussion in the Introduction of previous simulations of P3HT and other semiconducting polymers, including citing the recent papers mentioned by the referee, in order to put our work in context.

As the referee points out, a number of recent studies have used molecular dynamics simulations and electronic structure calculations of semiconducting polymers to determine the effects of the polymer structure on charge transport. Most of these works have focused on P3HT. However, as we point out in the introduction of the submitted paper, the structure of PBTTT had never been studied by molecular dynamics simulations at finite temperature until our current work.

We have added the following lines to the third paragraph of the introduction, just before "Although molecular mechanics ...":

"Recently, a number of studies have used molecular dynamics simulations and electronic structure calculations of semiconducting polymers [cite: Vukmirovic, J. Phys. Chem. B, 113, 409, 2009 and NanoLett, 9, 3996, 2009, Cheung, J Am Chem Soc, 131, 11169, 2009, Ruhle, J Chem Phys 2010, 132, 134103, Lan, Y.I. J. Phys. Chem. B, 2008, 112, 14857], in most cases P3HT, to determine the effects of the polymer structure on charge transport. However, ..."

2) Excluded-volume interactions, i.e. energetically unfavourable repulsive interactions, cause perpendicular alignment of closely spaced chains because, for a given separation between the chains, the atoms on the two chains can get furthest apart from each other if the chains are oriented perpendicular to each other, thus minimizing unfavorable repulsive interactions.

We have clarified this point by changing the sentence in which we refer to the excluded-volume interaction (lines 66-67, page 4) to "This minimum occurs because, for a given separation between two

chains, energetically unfavourable excluded-volume interactions are minimized when the chains pack perpendicular to one another, since the atoms on the two chains can get furthest apart from one another in this configuration; at very small separations, the repulsive interactions between the chains become so dominant that the chains can only pack perpendicular to one another. "

We have also modified the caption to Fig. 5 to make it clear that the distance r on the horizontal axis is the distance between the centers-of-mass of the sites defining the orientational vectors on different chains.

We also added several comparative sentences regarding the P1 first-rank orientational correlation function to the end of our discussion of the P2 correlation function.

3) We agree that the P1 first-rank orientational correlation function could, in principle, be a more useful measure of interdigitation. On the other hand, the P2 second-rank correlation function is more appropriate for the correlation function between normal vectors to the rings, since parallel and anti-parallel orientations are meaningless in this case.

However, it turns out that P1 is also not very useful for measuring sidechain interdigitation, for the following reason. If one considers the proposed crystal structure of PBTTT (Brocorens et al, Adv. Mater. 2009, 21, 1193-1198 - ref. 10 in the manuscript), even though the sidechains of nearest-neighbor polymer chains are interdigitated (and therefore anti-parallel: $P1(r) = -1$) in the plane of the thiophene and thienothiophene rings, in the ring-stacking direction the sidechains of nearest-neighbor polymer chains are parallel ($P1(r) = 1$) to one another and approximately the same distance apart as they are in the plane of the rings. Therefore the in-plane and out-of-plane nearest-neighbor contributions to $\langle P1(r) \rangle$ approximately cancel. We have confirmed that $\langle P1(r) \rangle$ is close to zero for all r for both P3HT and PBTTT.

As noted in our response to point (2), we have added several sentences after our discussion of our results for the P2 correlation function in which we state that P1 was calculated, but did not show anything because in-plane and out-of-plane nearest-neighbor contributions to $\langle P1(r) \rangle$ are expected to cancel.

4) As our simulations were for systems in the melt, we avoided a discussion about pretransitional ordering, since our systems still seem quite amorphous, even at the lowest temperatures.

5) We agree with the referee that our simple model of the effects of the polymer structure on intra-chain charge carrier mobility is too simplistic. We have therefore removed the section on the estimation of the intra-chain charge carrier mobility from the paper and added a qualitative discussion of the potential consequences of the intra-chain dihedral distributions measured in our simulations to page 4. In particular, we have added the lines:

"The relatively free rotation of the 1-6 dihedral could have negative consequences for the intra-chain charge carrier mobility in PBTTT, counteracting the beneficial effect on charge transport that the higher planarity of the 1-1 dihedral in PBTTT compared with P3HT would have on. This result suggests that the intra-chain charge mobility in PBTTT could be improved by hindering the rotation of the thienothiophene ring, for example by adding side chains to this ring (making sure not to eliminate the possibility of interdigitation of the dodecyl side chains on the thiophene rings, which is discussed below)."

We have also removed the paragraph at the end of the introduction that mentions these simple estimates of the intra-chain charge carrier mobility and replaced it with the lines:

"It is also found that, although PBTTT chains show an overall higher degree of planarity than P3HT chains, the planarity induced between adjacent thiophene rings in PBTTT by the bulky dodecyl side chains, which would lead to better intra-chain charge carrier mobility in PBTTT compared with P3HT, is somewhat compensated by the relatively free rotation about the bond joining the thiophene ring to the thienothiophene ring. This result suggests that the charge carrier mobility in PBTTT could be improved by adding side chains to the thienothiophene ring to hinder rotation about this bond."

6) We did not carry out any coarse-grained simulations in this work. We have defined coarse-grained site positions in terms of the centers-of-mass of groups of atoms in the atomistic systems simulated, in order to provide a short-hand naming convention for the parts of the P3HT and PBTTT monomers and to permit the calculation of the distribution functions in Figs. 3 to 5 that describe the key structural characteristics of the systems.

We have clarified this point by adding a sentence after the line in the main text of the article in which Fig. 1 is introduced (line 37-38, page 2) that states "Coarse-grained sites have been defined for the parts of the P3HT and PBTTT monomers in Fig. 1 in terms of the centers-of-mass of groups of atoms, in order to provide a short-hand naming convention for the parts of the P3HT and PBTTT monomers and to permit the calculation of various distribution functions, introduced below, which describe the key structural characteristics of the simulated systems."

A comparative MD study of the local structure of polymer semiconductors P3HT and PBTTT

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Atomistic molecular dynamics simulations of P3HT and PBTTT-C12 at finite temperatures are carried out to investigate the nanoscale structural properties that lead to higher measured hole mobility in PBTTT versus P3HT field-effect transistors. Simulations of the polymer melts show that the structural properties in PBTTT facilitate both intra- and inter-chain charge transport compared with P3HT due to greater degree of planarity, closer and more parallel stacking of the thiophene and thienothiophene rings, and possible interdigitation of the dodecyl side chains. The crucial role played by the bulky dodecyl side chain and thienothiophene ring, respectively, in determining *intra-chain* and *inter-chain* structural order is clarified.

1. Introduction

Organic conjugated semiconducting polymers have been extensively investigated due to their potential for large area roll-to-roll solution processing on flexible substrates at low cost.¹ Electronic and optoelectronic devices employing polymer semiconductors include solar cells, field-effect transistors (FETs), and light-emitting diodes (LEDs).² Two widely used polymers in these devices are poly(3-hexylthiophene) (P3HT) and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) due to their relatively high charge carrier mobilities. The device performance of these polymers is strongly dependent on the morphology, which has been shown to drastically affect charge transport properties in polymer electronics.³⁻⁴

Of the two polymers, PBTTT has recently attracted great interest due to its high hole mobility (0.2-0.6 cm² V⁻¹ s⁻¹ in long channels and 1.0 cm² V⁻¹ s⁻¹ in short channels)⁵⁻⁶ compared with that of P3HT (0.1-0.2 cm² V⁻¹ s⁻¹)⁷ as measured in FETs. In addition, the higher ionization potential of 5.1 eV (4.8 eV for P3HT) makes PBTTT more stable against oxidation by molecular oxygen in air.⁵ The higher hole mobility in PBTTT vs P3HT FETs has been attributed to greater mesoscale structural ordering, which leads to a smaller fraction of disordered domains that act as bottlenecks to charge transport, rather than to intrinsic electronic properties of the polymers.⁸ It has been estimated using *ab initio* density functional calculations that the hole mobility in the π - π stacking direction in crystalline PBTTT-C6 (PBTTT with alkyl side chains of 6 rather than 12 carbons) (15 cm² V⁻¹ s⁻¹) is lower than that in crystalline P3HT (31 cm² V⁻¹ s⁻¹) at room temperature.⁸ However, the measured hole mobility, which is expected to be limited by transport in the π - π stacking direction since intra-chain charge transport should be much faster,⁹ of P3HT and PBTTT in FETs shows the opposite trend, indicating that the two liquid crystalline polymers exhibit different structural characteristics. In particular, these results suggest that P3HT exhibits less nano-scale order than PBTTT.⁹ Furthermore, X-ray diffraction (XRD) measurements

and molecular modeling at zero temperature suggest interdigitation of the alkyl side chains of PBTTT¹⁰ but not of P3HT.¹¹

Atomic force microscopy (AFM) images have shown that upon annealing, PBTTT forms large areas of flat terraces of up to hundreds of nanometers.⁵ X-ray diffraction patterns also reveal distinctly sharper peaks for PBTTT than for P3HT, indicating greater crystallinity.^{5, 12} Furthermore, the ideal polymer-to-fullerene ratio in bulk-heterojunction solar cells is different for P3HT:PCBM (~1:1 w/w ratio) than for PBTTT:PCBM (~1:4 w/w ratio).¹³ This difference has been attributed to intercalation of PCBM between the side chains of PBTTT, a phenomenon which is sterically hindered in P3HT; as a consequence, PCBM only forms a separate electron-conducting phase at higher PCBM concentration with PBTTT than with P3HT.¹⁴ Experimental evidence for the molecular-scale structure of these polymers and their blends is indirect. Recently, a number of studies have used molecular dynamics simulations and electronic structure calculations of semiconducting polymers¹⁵⁻¹⁹, in most cases P3HT, to determine the effects of the polymer structure on charge transport. However, although molecular mechanics calculations have been carried out to determine minimum energy structures of crystalline PBTTT starting from crystalline initial configurations,¹⁰ no computational study of the molecular dynamics of PBTTT at finite temperature has been carried out to our knowledge. Computer simulations can not only help confirm the postulated structures determined from experiment, they can also help elucidate the detailed atomic-level mechanisms for the observed structures.

In this paper, we apply atomistic molecular dynamics (MD) of polymer melts to study the morphology in P3HT and PBTTT systems and to highlight the structural properties that lead to higher ordering in PBTTT. The structural properties of the polymer melt systems reveal that the longer dodecyl side chain on the PBTTT molecule is largely responsible for the observed highly ordered morphology as it hinders distortions of the polymer chain from planarity. The dodecyl side chain is also itself more ordered than the hexyl side chain in P3HT.

Radial distribution functions (RDFs) and orientational correlation functions (OCFs) of inter-chain sites, respectively, show that the thiophene and thienothiophene rings in PBTTT can approach each other more closely and orient more parallel with each other than the thiophene rings in P3HT, which would enhance inter-chain charge transport in the π - π stacking direction. It is also found that, although PBTTT chains show an overall higher degree of planarity than P3HT chains, the planarity induced between adjacent thiophene rings in PBTTT by the bulky dodecyl side chains, which would lead to better intra-chain charge carrier mobility in PBTTT compared with P3HT, is somewhat compensated by the relatively free rotation about the bond joining the thiophene ring to the thienothiophene ring. This result suggests that the charge carrier mobility in PBTTT could be improved by adding side chains to the thienothiophene ring to hinder rotation about this bond.

2. Computational Methods

Atomistic MD simulations were carried out using the LAMMPS molecular simulation package.²⁰ Simulation and molecular parameters (partial charges, bonds, angles, Lennard-Jones) were adapted from our earlier work,²¹ which was built upon the Marcon and Raos model for tetrathiophene.²² Dihedral potentials were based on *ab initio* calculations of P3HT oligomers by Sternberg and Darling.²³ All simulations were carried out at constant temperature and pressure (NPT ensemble) employing a Nosé-Hoover thermostat and Nosé-Hoover barostat. P3HT systems were simulated at temperatures of 500, 550, and 650 K while PBTTT systems were simulated at temperatures of 550, 600, and 650 K. The melting temperature of P3HT²⁴ and PBTTT²⁵ is approximately 500 K; thus the simulated systems were in the melt but, in some cases, close to the melting point. The simulation temperatures were chosen because simulating crystallization is more challenging from a computational standpoint. Furthermore, the melt close to the melting point should exhibit many of the structural characteristics of the solid. All simulations were carried out at 1 atm.

The molecular structures of P3HT and PBTTT are shown in Fig. 1. Coarse-grained sites have been defined for the parts of the P3HT and PBTTT monomers in Fig. 1 in terms of the centers-of-mass of groups of atoms, in order to provide a short-hand naming convention for the parts of the P3HT and PBTTT monomers and to permit the calculation of various distribution functions, introduced below, which describe the key structural characteristics of the simulated systems. The molecular parameters used for PBTTT in these simulations were transcribed from the P3HT molecule,²¹ and are given in the Supporting Information. The molecular parameters used for the thiophene rings and alkyl side chains on the PBTTT molecule were identical to those used for P3HT. For the fused thienothiophene ring, the groups of carbon-sulfur-carbon atoms had a net charge of zero and were assigned partial charges analogous to those of the corresponding atoms in the thiophene ring. The remaining pairs of carbon-hydrogen atoms had a net charge of zero and were assigned the same partial charges as the corresponding atoms in the thiophene

ring. An additional angle bending potential had to be set for the obtuse sulfur-carbon-carbon angle along the perimeter of the fused rings with a force constant taken from the OPLS-AA model²⁶ for an aromatic sulfur-carbon-carbon angle. The equilibrium angle was fixed by the planar geometry of the fused rings and the values of the other two angles at the carbon atom joining the rings.

The simulated P3HT systems contained 60 chains of 12 monomers per chain for a total of 18,120 atoms. The average

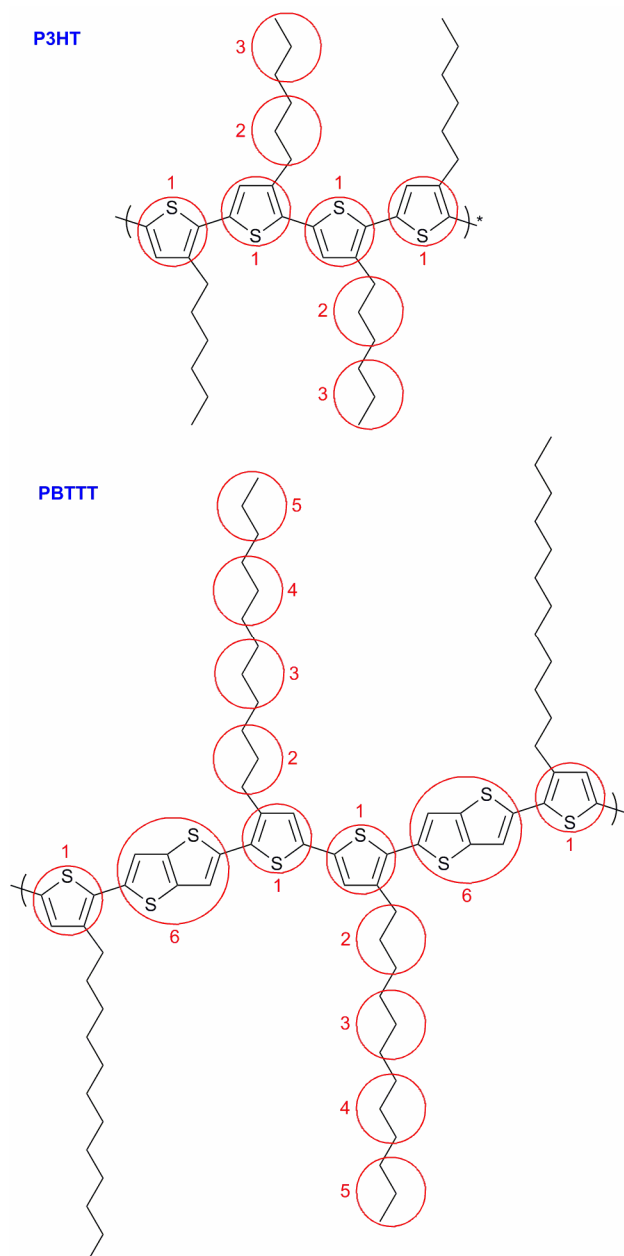


Fig. 1 Molecular structures of P3HT and PBTTT with coarse-grained site definitions taken as the center-of-mass of groups of circled atoms.

simulation box lengths were $\langle L \rangle = 60.5 \pm 0.1 \text{ \AA}$ (500 K), $61.4 \pm 0.2 \text{ \AA}$ (550 K), and $63.6 \pm 0.3 \text{ \AA}$ (650 K). PBTTT systems contained 50 chains of 4 monomers per chain for a total of 19,300 atoms. Average simulation box lengths were $\langle L \rangle = 61.9 \pm 0.2 \text{ \AA}$ (550 K), $62.9 \pm 0.2 \text{ \AA}$ (600 K), and $63.9 \pm 0.2 \text{ \AA}$

(650 K). Time steps for P3HT systems varied from 1.5 to 1.7 fs depending on the temperature, and time steps for PBTTT systems were 1.3 fs for all temperatures. The total simulation time at each temperature was based on the relaxation time of the autocorrelation function of the chain end-to-end vector $\mathbf{u}(t)$. For both systems, the simulations ran for at least $\sim 9\tau_2$, where $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle \sim \exp(-t/\tau_2)$ and $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial. Total simulation times varied between around 5 and 50 ns, depending on the temperature.

For structural distribution calculations, coarse-grained sites were defined by the centers-of-mass of groups of atoms, as shown in Fig. 1. Distribution functions and average properties such as the average squared end-to-end chain distance, $\langle R_{\text{end-to-end}}^2 \rangle$, were determined after equilibrium was ensured by confirming that the variables of interest fluctuated about average values.

3. Results and Discussion

The structural properties of P3HT and PBTTT melts were measured at the various simulated temperatures and are compared below for the common temperature of 550 K. Although the structural distributions at the other temperatures are for the most part not presented, they are qualitatively similar to those at 550 K, only slightly wider or narrower for higher or lower temperatures, respectively, as expected from thermal motion. For example, the dihedral distributions at 650 K are included in Fig. 2 and show only slight differences with the distributions at 550 K.

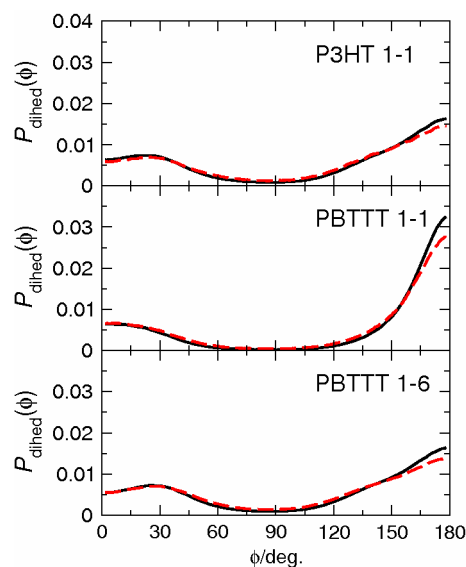


Fig. 2 The inter-ring sulfur-carbon-carbon-sulfur dihedral distributions for site pair 1-1 for P3HT and site pairs 1-1 and 1-6 for PBTTT at 550 K (solid) and 650 K (dashed).

The higher hole mobility measured in PBTTT vs P3HT FETs has been attributed to higher structural ordering of PBTTT into two-dimensional lamellar sheets.⁵ To quantify this planar structural ordering, the inter-ring sulfur-carbon-carbon-sulfur dihedral distributions were calculated between thiophene rings (site pair 1-1) and between thiophene and

thienothiophene rings (site pair 1-6) for the simulated polymer melt systems, as shown in Fig. 2. PBTTT shows a greater degree of planarity at 550 K for the 1-1 dihedral distribution, marked by the distinctly larger trans-to-cis ratio $\sim 6:1$ as opposed to $\sim 3:1$ in P3HT. The larger preference of the PBTTT 1-1 dihedral for the trans configuration and steeper drop-off of the dihedral distribution with deviations from the trans configuration allows for a more ordered planar arrangement that is more robust to deviations from planarity. Such distortions are expected to significantly impact intra-chain charge carrier mobility.⁸ Additionally, the larger preference for the trans configuration in PBTTT leads to main chains that are more stiff and stretched out. For the simulations at 550 K, PBTTT main chains have a Kuhn length $b = 33.1 \pm 1.0 \text{ \AA}$ as opposed to $b = 25.3 \pm 1.1 \text{ \AA}$ for P3HT. Here, the Kuhn length is defined as $b = \langle R_{\text{end-to-end}}^2 \rangle / R_{\text{max}}$, where R_{max} is the contour length of the chain. Polymer chains that are more stiff and stretched out, in addition to being more planar, are expected to yield higher structural ordering. The predominance of the trans configuration in PBTTT compared with P3HT is expected to be further accentuated at lower temperature and responsible for the observed large areas of flat terraces in AFM images of PBTTT.²⁷ The high degree of planarity facilitates both efficient intra-chain charge transport and inter-chain π - π stacking of thiophene and thienothiophene rings, which likely explains the higher hole mobility measured in PBTTT FETs.⁵⁻⁶

The larger preference of the PBTTT 1-1 dihedral for the trans configuration can be attributed to the dodecyl sidechains, which sterically hinder the torsion and the cis configuration. However, the PBTTT 1-6 dihedral shows similar shape and cis-to-trans ratio to the P3HT 1-1 dihedral. This indicates that the thienothiophene ring (site 6) rotates more freely and its torsion is less hindered, thus decreasing the overall degree of planarity of the PBTTT main chain. The relatively free rotation of the 1-6 dihedral could have negative consequences for the intra-chain charge carrier mobility in PBTTT, counteracting the beneficial effect on charge transport that the higher planarity of the 1-1 dihedral in PBTTT compared with P3HT would have on. This result suggests that the intra-chain charge mobility in PBTTT could be improved by hindering the rotation of the thienothiophene ring, for example by adding side chains to this ring (making sure not to eliminate the possibility of interdigitation of the dodecyl side chains on the thiophene rings, which is discussed below).

To see how the degree of planarity might facilitate inter-chain structural ordering, the radial distribution functions, $g(r)$, of inter-chain site pairs at 550 K were calculated, as shown in Fig. 3. Fig. 3a shows $g(r)$ for the thiophene-thiophene (site pair 1-1) in P3HT and PBTTT. The PBTTT 1-1 distribution shows a distinctly stronger correlation compared with the P3HT 1-1 distribution. The first peak at $r \approx 6 \text{ \AA}$ in PBTTT is significantly higher and sharper than that in P3HT. Fig. 3b shows $g(r)$ for main chain site pairs including the thienothiophene ring in PBTTT. Both the 1-6 and 6-6 distributions show strong correlations at both short and long ranges with peaks at $r \approx 6 \text{ \AA}$ and $r \approx 10 \text{ \AA}$. In the 6-6

distribution, there is even a weak peak at $r \approx 15$ Å. The substantially higher first peak for all the main chain RDFs of PBTTT compared with P3HT shows that the chains in PBTTT can approach each other more closely, permitting greater electronic overlap between chains, which would facilitate inter-chain charge transport that is most efficient if the rings π - π stack.

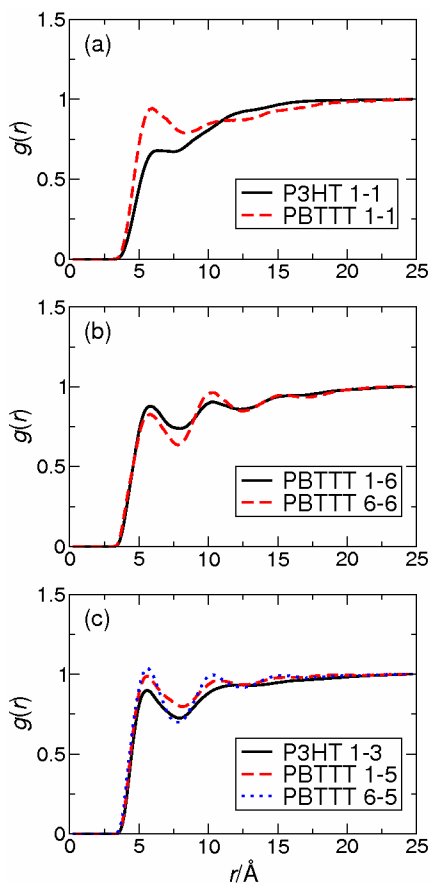


Fig. 3 Radial distribution functions for inter-chain site pairs at 550 K—(a) and (b); between main chain rings; (c) between main chain rings and end alkyl groups; r is the inter-site distance.

The structural characteristics of π - π stacking means that the inter-chain rings must align parallel to each other. Fig. 4 shows the orientational correlation functions for unit vectors normal to the main chain rings. The values close to 1 at short distances in all cases indicate parallel packing of the rings. This packing is most pronounced for the site pairs including a thienothiophene (site 6). This packing also extends to longer distances for the 6-6 site pair, as evidenced by the secondary peak at $r \approx 8$ Å, which is absent for the thiophene-thiophene (1-1) distributions of both P3HT and PBTTT. Although this peak is small, the fact that it is observable in the melt at 550 K is indicative of the crucial role the thienothiophene ring plays in inter-chain ordering in PBTTT.

The high structural ordering in PBTTT has also been partly attributed to interdigitation of the alkyl side chains.^{8, 10} To examine this phenomenon in our simulations, Fig. 3c shows $g(r)$ for the site pairs of main chain rings and end alkyl groups in P3HT and PBTTT. Both the PBTTT 1-5 and 6-5

distributions show stronger correlation than the P3HT 1-3 distribution. Of the two PBTTT distributions, the 6-5 shows a stronger correlation, as evidenced by the larger peaks and dips. In the 6-5 distribution, the strong first peak at $r \approx 6$ Å, which exceeds the bulk $g(r)$ value of 1, is possibly a sign of interdigitation between the dodecyl side chains, which has previously been demonstrated to be energetically favorable.⁸ The corresponding peak in the P3HT 1-3 distribution is below 1, indicating an absence of interdigitation.

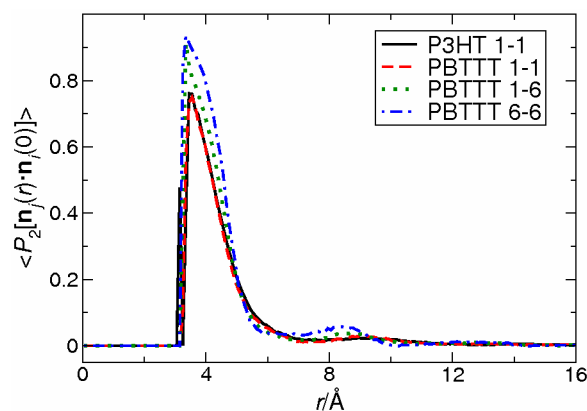


Fig. 4 Inter-chain orientational correlation functions for unit vectors normal to the main chain rings in P3HT and PBTTT at 550 K. P_2 is the second Legendre polynomial and r is the inter-site distance.

The presence of incipient interdigitation at 550 K in PBTTT is suggested by the inter-chain orientational correlation functions shown in Fig. 5 for unit vectors between coarse-grained sites consisting of triplets of adjacent carbon atoms (see Fig. 1 for site definitions) on the side chains. For both P3HT and PBTTT, the first minimum near $r \approx 4$ Å with a value close to $P_2 = -1/2$ indicates perpendicular packing (the opposite limit of $P_2 = 1$ would indicate parallel alignment). This minimum occurs because, for a given separation between two chains, energetically unfavourable excluded-volume interactions are minimized when the chains pack perpendicular to one another, since the atoms on the two chains can get furthest apart from one another in this configuration; at very small separations, the repulsive interactions between the chains become so dominant that the chains can only pack perpendicular to one another. The first peak at $r \approx 5$ Å is essentially the same for P3HT and PBTTT and shows parallel alignment between side chains. For the secondary minimum at $r \approx 8$ Å, PBTTT doesn't dip below zero while P3HT does, indicating that the side chains in PBTTT are more parallel with respect to each other than in P3HT. This result is consistent with experiment where XRD data has suggested that PBTTT side chains are more crystalline than P3HT side chains via interdigitation.¹⁰⁻¹¹ In addition, the Kuhn length was measured for the alkyl side chains in P3HT and PBTTT for our simulations at 550 K. The dodecyl side chains in PBTTT are more stiff and stretched out as characterized by a larger Kuhn length ($b = 8.9 \pm 0.2$ Å) than the hexyl side chains in P3HT ($b = 5.3 \pm 0.1$ Å). We also determined the P_1 inter-chain orientational correlation function (not shown), where P_1 is the first Legendre

polynomial. Although this correlation function can in principle distinguish between parallel ($P_1 = 1$) and anti-parallel/interdigitated ($P_1 = -1$) configurations of nearest-neighbor sidechains, it is not a discriminating measure of interdigitation when both parallel and anti-parallel nearest-neighbor sidechains are present. Based on the proposed crystal structure of PBTTT,¹⁰ even when PBTTT sidechains are interdigitated in the plane of the polymer backbone rings, nearest-neighbor sidechains in the ring-stacking direction of PBTTT are expected to be parallel and separated by roughly the same distance as the anti-parallel interdigitated sidechains in the plane of the rings. Therefore, the in-plane and out-of-plane contributions to the P_1 inter-chain orientational correlation function should cancel in PBTTT. In fact, we found that P_1 averaged to approximately zero at all distances for both P3HT and PBTTT.

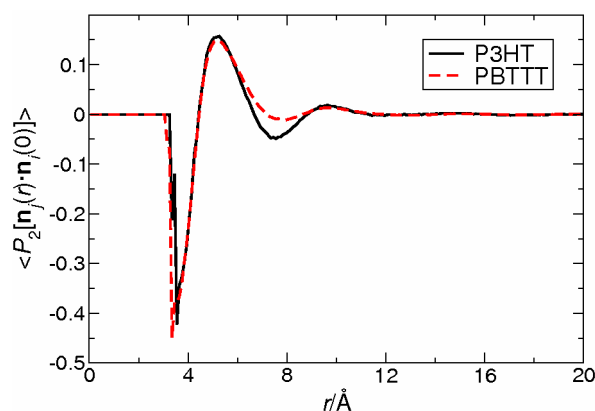


Fig. 5 Inter-chain orientational correlation function for P3HT and PBTTT alkyl side chains at 550 K. P_2 is the second Legendre polynomial and r is the distance between the centers-of-mass of the sites defining the orientational vectors on the different chains.

4. Conclusions

We have carried out the first atomistic molecular dynamics simulations at finite temperature of the semiconducting polymer PBTTT and compared its structure to another widely used semiconducting polymer, P3HT. Our simulation results support the hypothesis that the higher hole mobility measured in PBTTT vs P3HT FETs is due to the higher ordered morphology in PBTTT. In addition, our results provide evidence for possible molecular-level structural mechanisms for the differences in measured hole mobility. The dodecyl side chains prevent torsion of adjacent thiophene rings and are responsible for the overall high degree of planarity in PBTTT. The thienothiophene fused ring makes the main chain stiffer and allows closer packing and more parallel ring stacking due to its lack of side chains, which would improve *inter-chain* charge mobility. It also allows for interdigitation of the dodecyl side chains. However, the lack of side chains allows the thienothiophene ring to rotate more freely and disrupts the planarity of the polymer, counteracting the stiffness created by the dodecyl side chains, which could have a detrimental effect on *intra-chain* charge mobility. This indicates a delicate balance between competing molecular-level structural

characteristics of monomers making up the polymer. The structural order in PBTTT could potentially be improved by adding side chains to the thienothiophene ring to hinder its rotation.

Acknowledgments

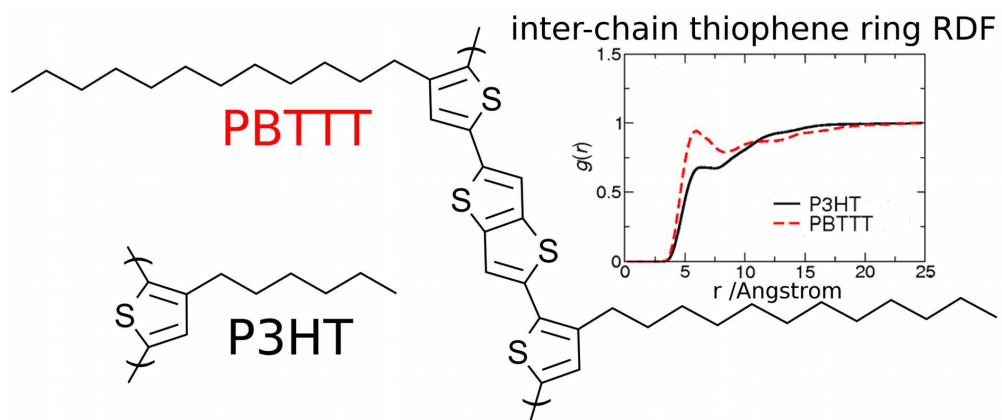
This material is based upon work supported by the Department of Energy under Award Number DE-FG36-08GO18018 and UC Davis start-up funding for AM.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: [Force-field details of PBTTT]. See DOI: 10.1039/b000000x/
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Supplementary Information for “A comparative MD study of the local structure of polymer semiconductors P3HT and PBTTT”

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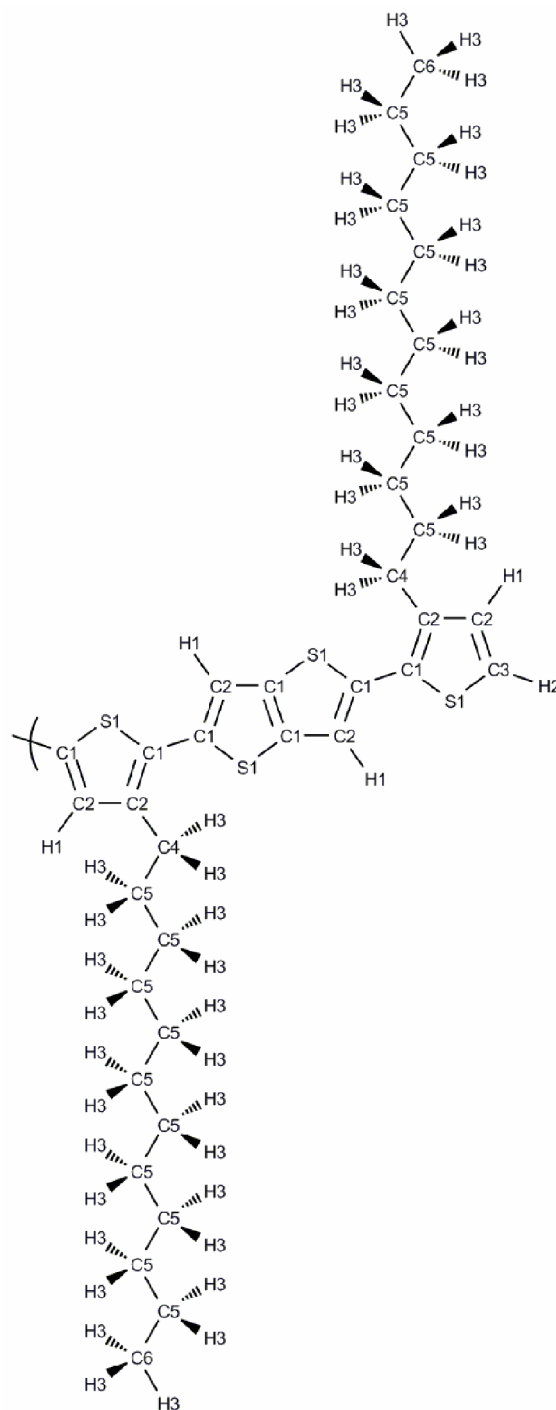


Fig. S1 Chemical structure of the end monomer in a poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) chain. Atoms of different type on our atomistic model are labelled with different numerical suffixes.

Table S1 Non-bonded parameters (LJ diameter σ_{ij} , LJ interaction strength ϵ_{ij} , and charge q_i) used in atomistic simulation models of PBTTT. PBTTT atom types are defined in Fig. S1.

Atom type i	$\sigma_{ij}/\text{\AA}$	$\epsilon_{ij}/\text{kcal mol}^{-1}$	q/e
S1 ^a	3.550	0.250	-0.1496
C1 ^a	3.550	0.070	0.0748
C2 ^a	3.550	0.070	-0.1817
C3 ^a	3.550	0.070	-0.1412
C4 ^b	3.500	0.066	0.0617
C5 ^c	3.500	0.066	-0.1200
C6 ^c	3.500	0.066	-0.1800
H1 ^a	2.420	0.030	0.1817
H2 ^a	2.420	0.030	0.2160
H3 ^c	2.500	0.030	0.0600

^a Adapted from Ref. [1] (see our previous work for details [3]), with LJ parameters from OPLS-AA model [2].

^b From OPLS-AA model [2], with charge adjusted for monomer neutrality.

^c From OPLS-AA model [2].

Table S2 Parameters used in harmonic bond length potential $V_{\text{bond}}(l) = k_l(l - l_0)^2/2$ in atomistic simulation models of PBTTT. PBTTT atom types are defined in Fig. S1.

Bond type	$l_0/\text{\AA}$	$k_l/\text{kcal mol}^{-1} \text{\AA}^{-2}$
S1-C1 ^a	1.732	582.50
C1-C2 ^a	1.364	1028.54
C2-C2 ^a	1.428	906.20
C2-H1 ^a	1.080	741.26
C1-C1 ^a	1.430	784.58
C3-H2 ^a	1.080	741.26
C2-C4 ^b	1.510	634.00
C4/C5-C5/C6 ^b	1.529	536.00
C4/C5/C6-H3 ^b	1.090	680.00

^a Adapted from Ref. [1] (see our previous work for details [3]).

^b From Ref. [2].

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Table S3 Parameters used in harmonic bond angle potential $V_{\text{angle}}(\theta) = k_\theta(\theta - \theta_0)^2/2$ in atomistic simulation models of PBTTT. PBTTT atom types are defined in Fig. S1.

Angle type	$\theta_0/\text{deg.}$	$k_\theta/\text{kcal mol}^{-1} \text{rad}^{-2}$
C1-S1-C1 ^a	92.774	172.720
S1-C1-C2 ^a	110.292	172.720
C1-C2-C2 ^a	113.322	79.164
C2-C2-H1 ^a	123.700	70.526
C2-C1-C1 ^a	130.140	109.388
C2-C3-H2 ^a	125.100	70.526
C1-C2-H1 ^a	122.979	70.526
S1-C1-C1 ^a	119.569	83.480
S1-C3-H2 ^a	124.609	57.574
C2-C2-C4 ^b	123.700	140.000
C1-C2-C4 ^b	122.979	140.000
C2-C4-C5 ^c	114.000	126.000
C2-C4-H3 ^c	109.500	70.000
C4/C5-C5-C5/C6 ^c	112.700	116.700
C4/C5/C6-C4/C5/C6-H3 ^c	110.700	75.000
H3-C4/C5/C6-H3 ^c	107.800	66.000

^a Adapted from Ref. [1] (see our previous work for details [3]).

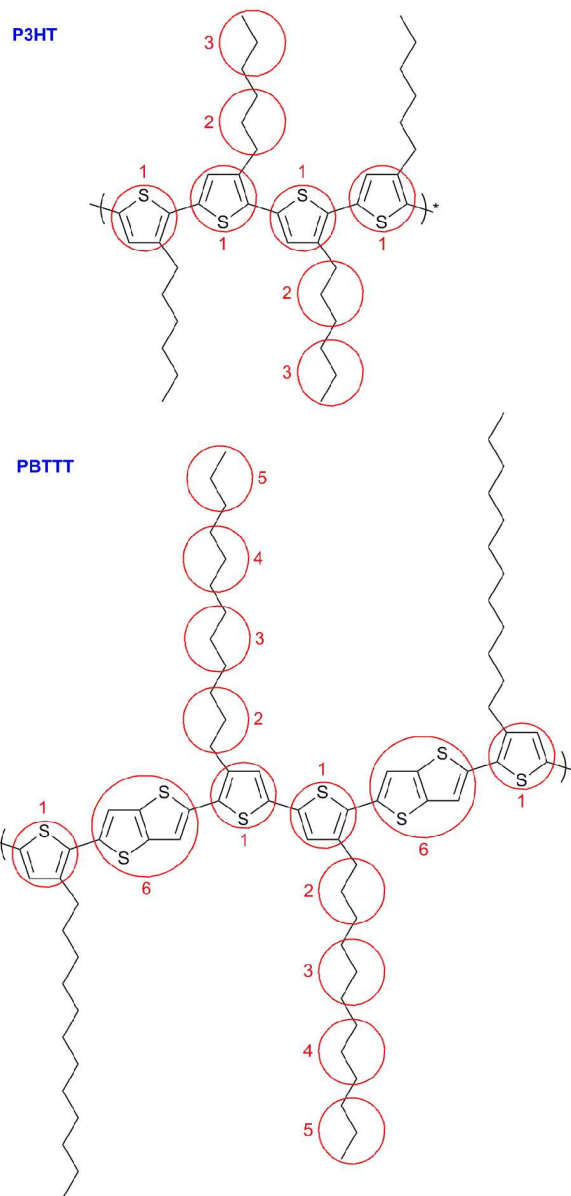
^b θ_0 adapted from Ref. [1]; k_θ from Ref. [2].

^c From Ref. [2].

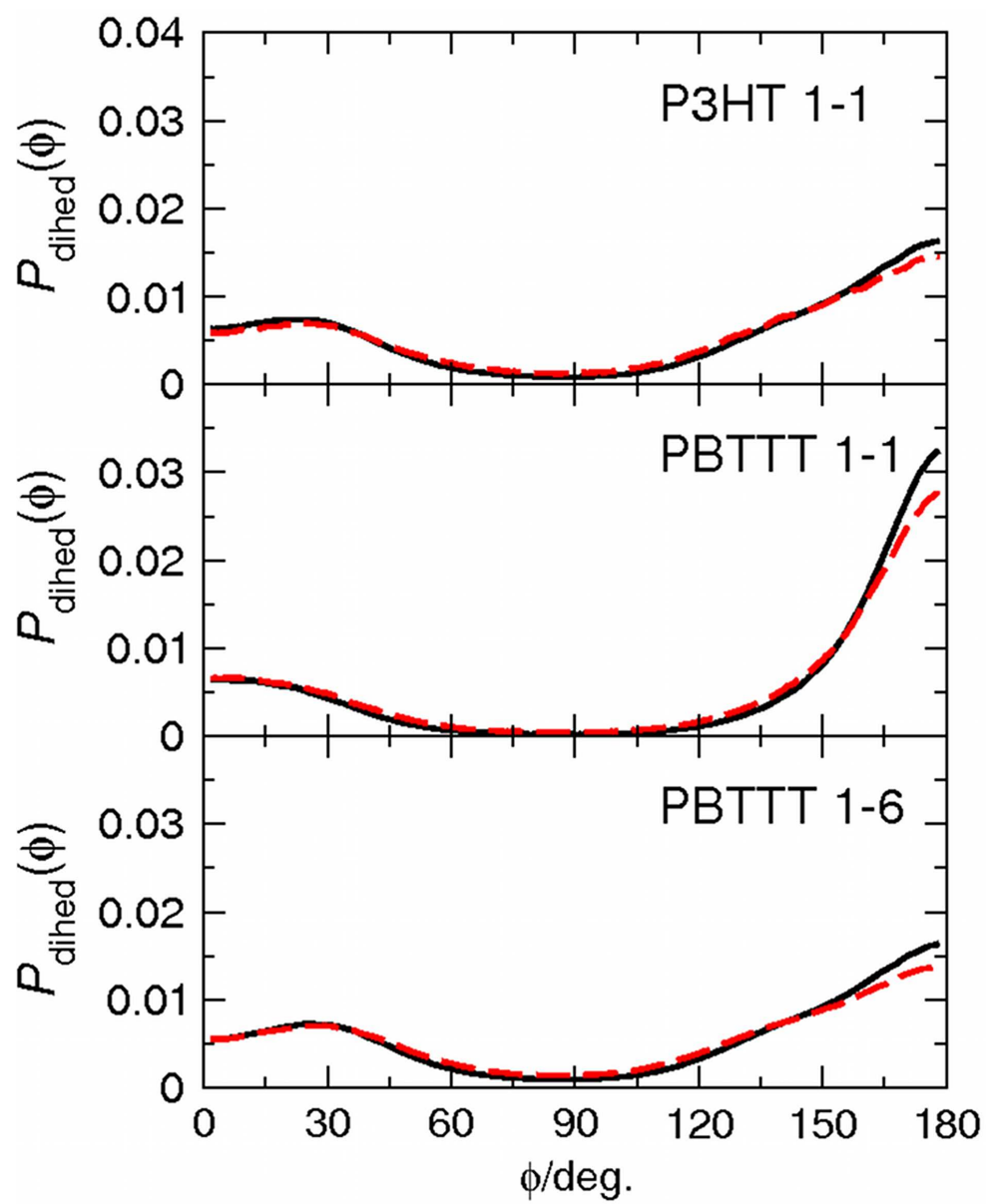
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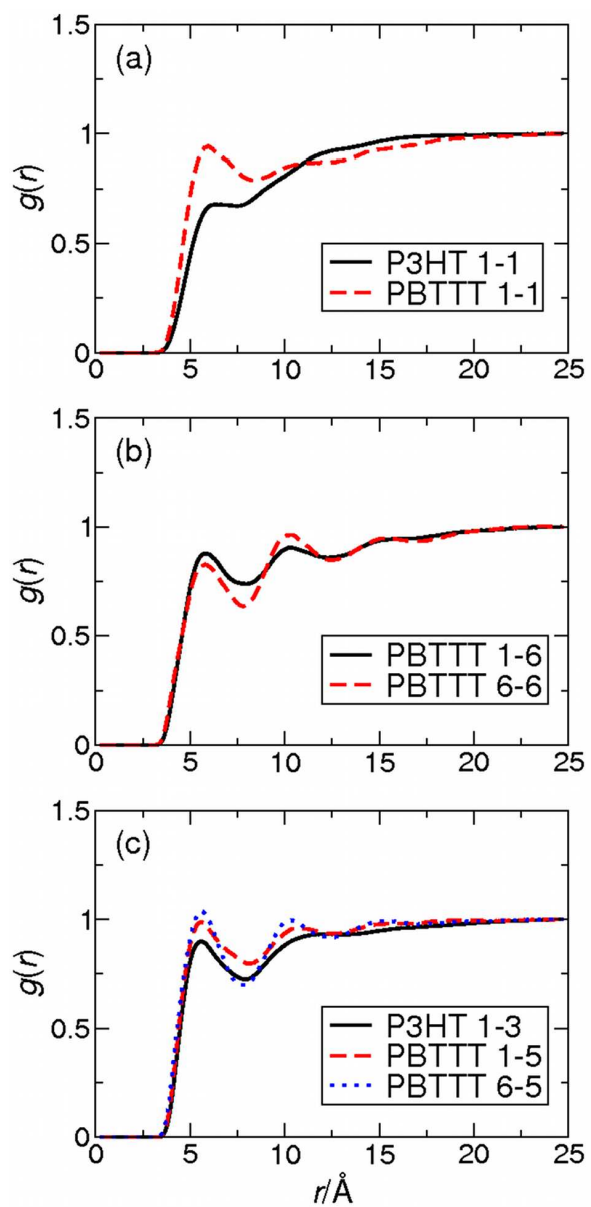
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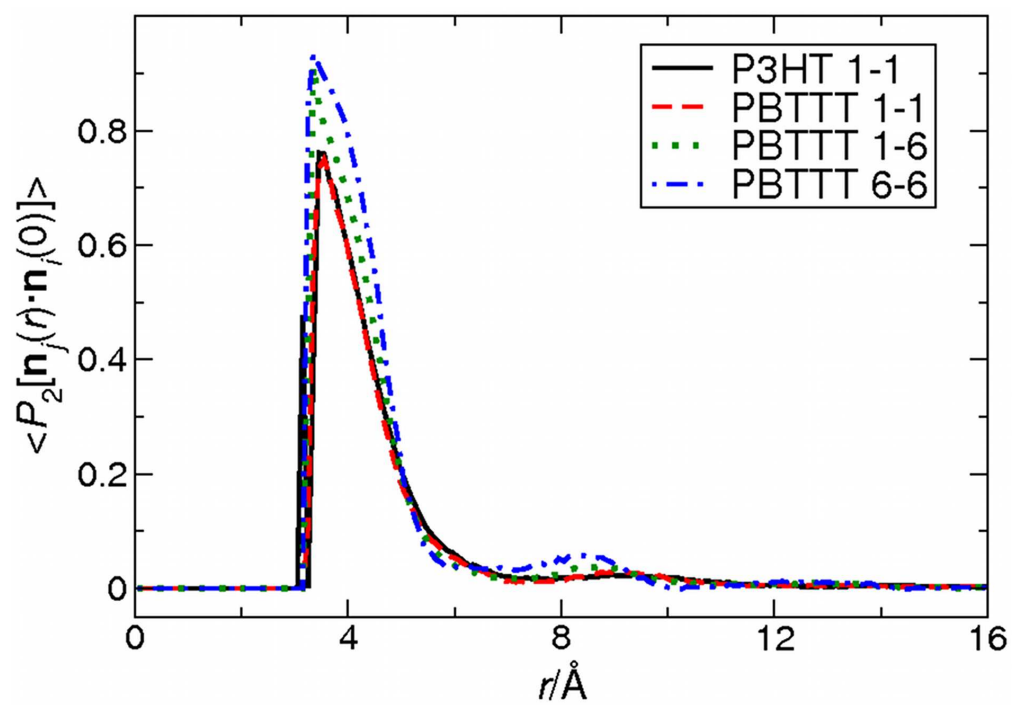
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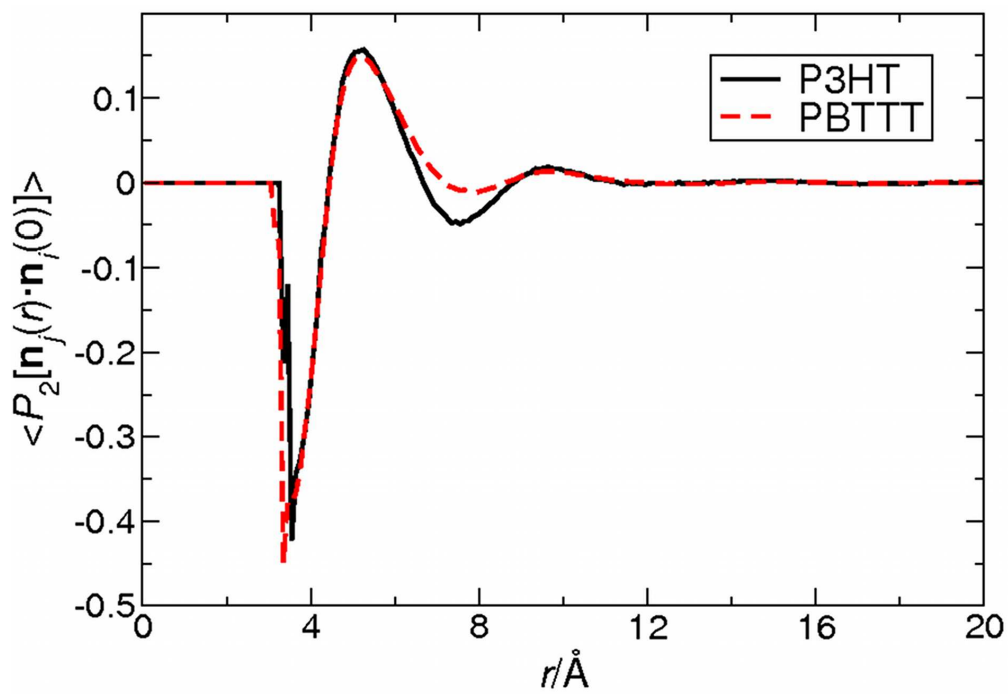
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