Abstract

Crystal structure of conjugated molecules and polymers is fundamentally critical to understand their multilevel microstructures, carrier transport, and diverse functions. However, to determine the crystal structure of conjugated polymers is a significant challenge, mainly due to the poor crystallinity, weak diffraction, and instability under high-energy radiation. Here, we build the possible crystal structures of eight typical conjugated polymers, covering several widely used molecular segments in organic optoelectronics. We model the packing structures of these seed polymers based on synchrotron X-ray diffractions and molecular simulations. These crystal structures provide a new platform to predict the packing structures of more related polymer systems, extending the molecular scope. Based on this polymer crystal structure database, the multiscale microstructures and charge transport properties of conjugated polymers can be predicted before experiments. This study sets up a polymer crystal structure database to eliminate the current trial-and-error approaches and accelerating the design of high-performance conjugated polymers.

KEYWORDS
charge transport, conjugated polymers, crystal structure, molecular modeling

1 | INTRODUCTION

Conjugated polymers demonstrate a bright future due to their applications in energy conversion, flexible electronics, bioelectronics, and so forth.1–5 However, lacking crystal structures of conjugated polymers limits the fundamental understanding of the multiscale structure–property relationship and the development of high-performance polymer-based devices.6 Previous studies on the microstructures of conjugated polymers usually depend on X-ray scattering and diffraction techniques. X-ray techniques typically provide the coarse packing models of conjugated polymers and seldom offer atomic-level packing structures, which is critical to revealing the structure–property relationships in the polymer systems. The current analysis of structure–property relationships of conjugated polymers requires time-consuming synthesis and complex structural characterization. On the other hand, such a process often...
provides case-dependent design strategy, mainly due to the indistinct structural information of conjugated polymers. Lacking precise crystal structures of conjugated polymers results in this current trial-and-error approach, significantly limiting the establishment of a complete description from chemical structures to device performance of conjugated polymers. Single crystals of conjugated molecules and polymers are usually considered as ideal platforms to investigate their structure–property relationships at atomic levels. However, polymer crystals usually comprise unavoidable packing defects and numerous grain boundaries, harming the achievement of high-quality polymer crystals and crystal structures. Only a few instances were reported about the conjugated polymer crystals, charge transport, and structure elucidation. Therefore, it is urgent to build a crystal structure database (CSD) of conjugated polymers.

The crystal structures of conjugated polymers cannot be precisely determined due to the polymer weight distribution and unavoidable packing disorders, leading to weak diffraction and remarkable radiation damage. Usually, a combination scheme of theoretical molecular simulations with experimental structural constraints has been demonstrated to achieve the possible crystal structures. Structural constraints can be extracted from nuclear magnetic resonance (NMR), X-ray diffraction and scattering, and so forth, including hydrogen–hydrogen distances and lattice parameters. However, only one or a few polymers with similar backbones were reported, such as thiophene-based polymers and polyfluorenes; no general conjugated polymer CSD was demonstrated up to date.

Poly(3-alkylthiophene) (P3HT) is a variety of well-defined conjugated polymers, especially for P3HT. Brinkmann et al. determined the possible structural model of P3HT with a P21/c space group using electron diffractions. Hansen and coworkers reported the crystal structures of P3HT by combining the PXRD and solid-state NMR, although Hansen’s structural model of P3HT is different from Brinkmann’s model. It should be noted that the crystal structures of conjugated polymers might be sensitive to the different experimental conditions, such as molecular weight and crystallization conditions. In this study, we adopted posttreatment of eight widely used conjugated polymers to enhance molecular packing and then performed powder X-ray diffraction (PXRD) with synchrotron radiation. Based on the experimentally observed PXRD patterns and hypothesized packing models, reasonable crystal structures of eight seed polymers were provided. From these seed structures, polymer with similar molecular segments can be well predicted, offering an opportunity to broaden the structure scope of the polymer CSD. To the best of our knowledge, this study firstly established a general CSD for conjugated polymers, which will deepen the microscopic understanding at atomic levels. With the precise polymer crystal structures in hands, the materials research community can break through the old trial-and-error approach and achieve in-depth molecular understanding for developing high-performance polymers.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Diketopyrrolopyrole (DPP); naphthalene diimide (NDI); isindigo (IID); benzodifurandione-based oligo(p-phenylene vinylene) (BDOPV); P3HT; poly[(4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diy]-3-fluoro-2-{(2-ethylhexyl)carbonyl}thienol[3,4-b]-thiophenediyl] (PTB7); poly[N-9’-hepta-decanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)] (PCDTBT); and poly [N,N’-bis(2-octyldecydiyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5’-(2,2’-bithiophene)] (P(NDI2OD-T2)). P3HT (Mn = 42.8 kD, PDI = 2.19), PCDTBT (Mn = 66.0 kD, PDI = 2.08), and PTB7 (Mn = 12.7 kD, PDI = 1.95) were purchased from Luminescence Technology Corp. IID2T (Mn = 74.7 kD, PDI = 1.60), DPP4T (Mn = 75.6 kD, PDI = 3.43), P(NDI2OD-T2) (Mn = 105.4 kD, PDI = 1.90), FBDDPPV (Mn = 31.7 kD, PDI = 4.95), and BDOPV-2T (Mn = 94.6 kD, PDI = 4.51) were synthesized according to the previously reported procedures. The molecular weights were evaluated using Polymer Laboratories PL-GPC220 with 1,2,4-trichlorobenzene as eluent at 150°C and polystyrene standards for molecular weight calibration. Polymer powder was tableted to exclude the microvoids for density measurement. The polymer density was estimated with the mass and volume.

2.2 | X-ray diffraction

PXRD was carried out at the beamline BL17B1 of the Shanghai Synchrotron Radiation Facility (SSRF) with the X-ray wavelength of 0.8266 Å, equipped with an MD2 diffractor and Rayonix MX300 detector. The diffraction experiments were performed with a liquid nitrogen cooling system. For each sample, 36 diffraction patterns of different incident angles were merged for data completion and enhanced intensity. Accordingly, 1D PXRD profiles were integrated along the radial direction and plotted against 2θ. Pawley refinement of the PXRD data was performed with the simulated crystal structure, where the Pseudo-Voigt function was applied for peak profile fitting.
2.3 Molecular modeling and simulation

Molecular geometries of the polymeric repeating units were optimized at the B3LYP-D3/def2-SVP level of theory with ORCA 4.2.0 package. Alkyl chains were carefully set with fully extended conformation and interdigitated structures for branching side chains. The cell parameters were initialized according to the PXRD data. The crystal structures were optimized with Dreiding force field and the atomic partial charges were assigned using the charge equilibration (QEq) approach. The relaxed structure was subjected to a quenched molecular dynamics simulation (NPT, 1 ns, \( P = 1 \text{ atm}, \ T = 300 \text{ K} \), quench frequency = 10 ps) followed by a long molecular dynamics simulation (NPT, 5 ns, \( P = 1 \text{ atm}, \ T = 300 \text{ K} \)). All molecular dynamics simulations were performed with Materials Studio package. Dreiding force field, QEq charges, velocity scale thermostat, Berendsen pressure coupling, and a time step of 2 fs were adopted during these simulations. Reasonable crystal structures of each polymer were selected according to the calculated total potential energy and experimental PXRD results. To improve the accuracy of the atomic positions, self-consistent charge density-functional tight-binding (SCC-DFTB) was employed to further optimize the atomic positions with the fixed cell parameters. The 3ob Slater-Koster atomic parameters were used in DFTB calculations except the Se-containing polymers. The transfer integrals between adjacent backbones were calculated at the B3LYP-D3/def2-SVP level of theory with ORCA 4.2.0 package. The crystal structures of eight seed polymers and sixteen DPP-based polymers are provided in Protein Data Bank (PDB) files in Online Supporting Information. CCDC 2074820 and 2074829–20374835 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

3 RESULTS AND DISCUSSION

3.1 Polymer scope

Eight conjugated polymers (Figure 1) were selected as seed polymers, including the molecular segments of oligothiophene, DPP, NDI, IID, and BDOPV. These polymeric and molecular segments have been widely used in optoelectronic devices including organic field-effect transistors, solar cells, thermoelectrics, and so forth. First, we built the polymer packing structures according to the lattice parameters from synchrotron X-ray diffractions. Then, crystal structures were optimized with molecular mechanics and quantum mechanics simulations. From the crystal structures of these eight seed polymers, it is facile to obtain more crystal structures of the other related conjugated polymers. That is, a self-contained CSD of conjugated polymers can be founded and updated with ongoing efforts. Finally, we provided a tutorial example of 16 DPP-based polymers by examining the relationship between electronic coupling and measured mobilities. Moreover, traditional approaches to develop novel conjugated polymers are almost trial-and-error and case dependent. Our polymer CSD can be used for predicting the packing structures and optoelectronic properties of conjugated polymers, helping to evaluate the molecular design strategy before experiments.

FIGURE 1 Chemical structures of eight seed conjugated polymers involved in this study
3.2 X-ray diffraction and crystal structures

To acquire high-quality X-ray diffraction data, the polymer samples were treated by thermal annealing, solvent vapor annealing (SVA), or without posttreatment (pristine): P3HT, PCDTBT, PTB7, IID2T, DPP4T, P(NDI2OD-T2), FBDPPV, and BDOPV-2T (Figure 1). We collected the PXRD patterns of each polymer sample with synchrotron radiation due to the high brilliance and flux (Figure 2). It is noted that conjugated polymer powders exhibited strong X-ray absorption, making it challenging to obtain high signal-to-noise ratio diffraction patterns using the laboratory-level X-ray source. Besides, liquid nitrogen flow was adopted to cool the polymer sample, reducing scattering damage and thermal fluctuation. To enhance the signal intensity and data completeness, 36 diffraction patterns from different angles were emerged for each polymer (Figure S1). According to the PXRD results, seven polymers except PCDTBT exhibited strong diffractions with clearly observed peaks. P3HT, PTB7, IID2T, and FBDPPV showed similar PXRD profiles before and after thermal annealing or SVA, respectively, while DPP4T and BDOPV-2T showed enhanced diffraction peaks after thermal annealing and SVA. In contrast, PCDTBT only exhibited weak diffraction features with

**FIGURE 2** Synchrotron radiation powder X-ray diffraction (PXRD) of these eight seed conjugated polymers (up: 2D patterns; down: 1D profiles). The polymer samples were treated with different conditions: pristine, thermal annealing, and solvent vapor annealing (SVA). The X-ray wavelength is 0.8266 Å. Lamellar and π-π diffraction peaks are labeled in the 1D profiles. The typical π-π stacking distances of 3.4 to 3.6 Å loads in the 2θ of 14.0 to 13.2°.
two broad peaks even after thermal annealing, which is consistent with the previously reported disordered packing structures of PCDTBT.43

According to the PXRD results and the chemical structures, orthorhombic unit cells were built for every polymer. The molecular segments were carefully set in the unit cell with several structural constraints including planar conjugated backbone, tightly stacked side chains with extended conformation, and dense molecular packing. During the initial molecular modeling, the following aspects were considered: (1) The cis-trans configuration between conjugated moieties and relative orientations of stacked polymer chains might lead to different polymer packing structures.8 Here, we consider the situation of trans configuration while other structural configurations can be easily obtained by modified our reported crystal structures; (2) According to the previous theoretical simulations by Lemaur et al.,44 the stereochemical centers of the branched alkyl chains in P(ND12OD-T2) only weakly affect the polymer packing motifs. Therefore, the stereochemical centers of the branched alkyl chains are regarded as mesomer (R/S); (3) All the initial crystal structures of eight conjugated polymers are set as orthogonal crystal systems with three-dimensional periodic boundary conditions. Although high cell symmetry can be reached in several polymers, conjugated polymers possess more complex structures and packing disorders. Based on the above considerations, we built the crystal packing structures of each polymer with trans-backbones and extended-conformation side chains (Figures S2 and S3). These initial crystal structures were optimized and then submitted to the molecular dynamics simulations to reach possible packing configurations. During the geometry optimization and molecular dynamics simulations, all atomic positions and cell parameters are free to reach energetically favorable structures. Importantly, no additional symmetry was applied during the whole molecular modeling; consequently, all the polymer cells finally transited to the energetically favorable triclinic crystal systems.50

The searched crystal structures were screened according to the energy ranking and experimental lattice parameters from PXRD. Furthermore, the most energetically favorable crystal structures with reasonable density and lattice parameters were selected. The finally optimized crystal structures (Figure 3 and Tables S1–8) possessed narrow density distribution (Figure S4) from sampling molecular dynamics simulations. The crystal structures of eight seed polymers exhibited similar density against measured values with relative error ranging from 2%–11% (Table S9), supporting the polymer packing structures are reasonable. These polymer crystal structures yielded simulated PXRD patterns in good agreement with experimental results (Figure S5). Pawley’s refinement of the PXRD profiles reproduced the experimental diffraction curves with minor residual errors, supporting our modeled polymer crystal structures are reliable (Figure S6).

To improve the accuracy of the atomic positions, we employed density functional-based tight-binding (DFTB) calculations to finally optimize the atomic positions in the polymer crystal structures.57 During this step of DFTB calculations, the lattice parameters of the polymer crystals were fixed at the values from molecular dynamics simulations. These finally optimized crystal structures of the eight seed polymers are provided as supplementary files for extending the material scope as the structures can be easily modified. It should be noted that conjugated polymers might form different packing structures under different crystallization conditions, such as lattice variation and packing dislocation. For example, P3HT exhibited various polymorphs with different packing modes and lattice parameters;18,19 PCDTBT adopt bilayer motif in crystalline phase;45 P(ND12OD-T2) showed segregated and mixed interchain stacking in the aligned thin-films.46 These varied polymer packing structures can be simply founded using the related crystal structures. Although the real situation might be complicated for conjugated polymers, our polymer CSD provides an opportunity to modify the crystal structures according to the experimentally observed structure constraints. Moreover, using the crystal structures as the initial structural models, disordered and even amorphous models can be derived, such as expanding the periodic boundary conditions to supercells and thermally disturbing the tight packing structures. The derived structural models are critical for understanding the effect of packing structures on related charge transport properties in real polymeric systems.47,48

3.3 Crystal structure validation

DPP is a widely used molecular motif in the chemical dye and the active materials for field-effect transistors, solar cells, thermoelectrics, and so forth.49–52 Hence, we predicted the crystal structures of 16 DPP-related polymers and further investigated the charge transport features. Starting from the crystal structure of DPP4T, structure models of 16 DPP-related polymers were predicted; and the impact of molecular packing on charge transport was studied (Figure 4A). These 16 DPP-based polymers included various
aromatic linkers and copolymer units, including furan, thiophene, selenophene, pyridine units, and so forth. The DPP4T’s original crystal structure was modified according to the molecular geometry of each derivative. The modified crystal structures were then reoptimized to provide stable packing models.

According to the Marcus theory, the intermolecular charge hopping rate in organic semiconductors can be related to two parameters: reorganization energy and transfer integral (i.e., electronic coupling). 53 The reorganization energy usually originates from the ionization-induced geometrical reorganization plus the energy change in polarization of the surrounding molecules; the reorganization energy retains similar values for related derivatives. 54 The transfer integrals between the adjacent π-stacking dimer were estimated using density-functional theory calculations (Figures 4B and S7). The measured mobilities of these 16 DPP-based polymers were gathered for comparison (Table S10). We found that the literature-reported mobility exhibited a preferably positive relationship against the calculated transfer integral (Figure 4C), 59,50 although the experimental mobility is affected by several device issues, such as contact resistance and charge trapping. According to the relationship between molecular

**FIGURE 3** Crystal structures of these eight seed conjugated polymers. (A) P3HT. (B) PCDTBT. (C) PTB7. (D) IID2T. (E) DPP4T. (F) P(NDI2OD-T2). (G) FBDPPV. (H) BDOPV-2T. The crystal structures are visualized with Corey–Pauling–Koltun (CPK) models. Both top view (along b axis) and side view (along c axis) are illustrated to demonstrate the lamellar and π–π stacking, respectively. Gray: C; white: H; red: O; blue N; olive: F; yellow: S. BDOPV-2T, benzodifurandione-based oligo(p-phenylene vinylene)-2T; DPP, diketopyrrolopyrrole; IID2T, isoidigo; P3HT, poly(3-hexylthiophene); PCDTBT, poly[N-9’-hepta-decanyl-2,7-carbazole-alt-5,5-(4’4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)]; PTB7, poly([4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl]3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl])
segments and charge transport parameters (Figure 4C), DPP4, DPP5, and DPP14 possessed larger interchain transfer integrals, facilitating charge transport. The large interchain transfer integrals in the polymer systems imply that both dithiophenylethene and pyridine motifs might be the profitable chemical groups for efficient charge transport in conjugated polymers. The enhanced intrachain delocalization and interchain electronic coupling would benefit the overall charge transport. This significant correlation between simulated transfer integral and measured mobility validates the feasibility of our polymer CSD in understanding and even predicting the charge transport properties of conjugated polymers. We note that the CSD with eight seed polymers covers the numerous molecular segments of conjugated polymers; hence, other polymer crystal structures can be easily derived from the eight seed polymers. Therefore, we believe that the CSD provides an opportunity to predict polymer crystal structures and screen their charge transport properties.

## CONCLUSIONS

In summary, the atomic-level crystal structures of eight widely used conjugated polymers as the seeds have been successfully elucidated by combining molecular simulation, quantum chemical calculations, and X-ray diffractions. Accordingly, we have built a CSD containing eight seed conjugated polymers, which can be easily extended to other polymer systems. Their atomic-level crystal structures are fundamentally critical to bringing the molecular structures to supramolecular organizations in real polymeric films and bulks. Furthermore, the predicted polymer packing structures based on the CSD correlate well between carrier transport mobility and interchain transfer integrals. Our work provides a polymer CSD, eliminating the traditional trial-and-error approaches and accelerating the design and characterization of conjugated polymers. Such polymer CSD can be easily modified and updated. This may allow, for example, predicting the polymer crystal structures before synthesis and characterization experiments, as well as the large-scale computational screening of polymer structures for...

![Figure 4](image-url)
electronic functions using machine learning and artificial intelligence. We envision that the polymer CSD will offer structural solutions and insights to the currently unsolved problems where the atomic-level supramolecular packing organization is required.

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CONFLICT OF INTERESTS
The authors declare no conflict of interest.

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