Controlled steric selectivity in molecular doping towards closest-packed supramolecular conductors

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Recent developments in molecular doping technologies allow extremely high carrier densities in polymeric semiconductors, exhibiting great diversity because of the unique size, conformation, and steric effect of molecular dopants. However, it is controversial how steric effects can limit the doping efficiency and to what extent dopants can be accommodated in polymers. Here, we employ two distinct conjugated polymers with different alkyl side-chain densities, where polymers are doped via anion-change, allowing greater variation in the incorporation of molecular dopants having different electrostatic potentials and shapes. We characterize the doping efficiency with regard to steric effects, considering the unique void space in the conjugated polymers. Our study reveals that doping efficiency of polymers with sparse alkyl side-chains is significantly greater than that with dense side-chains. A closest-packed supramolecule is realized with a particular combination of a sparse polymer and a large dopant, giving rise to high conductivity, air stability, and remarkably high work function. This work provides a critical insight into overcoming steric effects in molecular doping.

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Impurity doping is one of the most important semiconductor processes, by which (opto)electronic properties can be tuned precisely\(^1\). A dopant, that is, either an electron donor or an acceptor, is incorporated into a semiconductor medium and can shift the Fermi energy. The concept of impurity doping, already established in silicon electronics, has been extended to organic semiconductors (OSC), where molecular dopants rather than atomic dopants are important agents in chemical reactions\(^3\). Various dopants and processes have been utilized to achieve efficient chemical doping of OSCs, particularly for p-type doping. Here, an integer electron transfer occurs when a redox reaction between a \(\pi\)-conjugated polymer and a dopant is energetically favorable, resulting in a donor–acceptor association. Recently, relatively high doping levels in polymeric semiconductors have been realized via various molecular doping methods, such as chemical engineering utilizing self-compensation by covalent bounded counter-ions\(^9\), photo-doping\(^12\), and solid-state diffusion\(^13\). As well as possibly via double doping\(^17\). Of these methods, extremely high carrier density with the charge density per unit volume of \(10^{21}\) cm\(^{-3}\) in polymeric semiconductors can be achieved via anion-exchange doping\(^18,19\). In anion-exchange doping, a host–guest system also includes a large excess of a salt (consisting of a cation, and an anion). A conventional p-type doping is initiated by an acceptor dopant (e.g., 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane; F\(_4\)TCNQ), resulting in the formation of intermediate [polymer+F\(_4\)TCNQ\(^{2-}\)]. The second anions that are supplied by the additional salt are instantaneously exchanged with F\(_4\)TCNQ\(^{2-}\). The intermediate consisting of F\(_4\)TCNQ is exchanged to the secondary ion pair via anion exchange, where the intermediate is likely to undergo full integer charge transfer. Anion-exchange doping uses ionic interactions as a driving force to promote doping levels, and allows an anion-exchange efficiency of nearly 100% when an optimum salt is used. A critical difference of anion-exchange doping from conventional molecular doping is that the resulting dopant incorporated in the \(\pi\)-conjugated polymers does not necessarily initiate redox reaction; the initial electron transfer can be triggered by conventional, redox-active dopants, and the anion exchange process is then followed to form the secondary donor–acceptor pair. This functional separation may facilitate a novel host–guest structure that has not been achieved by conventional doping, suggesting that there are opportunities to explore functional host–guest systems, which will allow a greater variation of molecular dopants having different electrostatic potentials/shapes to be incorporated into polymeric semiconductors. In particular, steric effects of molecular dopants in hybrid host–guest systems would be investigated systematically.

Until now, high doping levels have been achieved only to a limited extent in semicrystalline, polymeric semiconductors\(^13,16,18,19\). This may be because spatially confined donor–acceptor association is only established within restricted regions in semi-crystalline polymers\(^13,15\), where molecular dopants are intercalated specifically into nanometer-sized voids that are likely to be alkyl side-chain regions. The most critical factor driving molecular doping is likely to be the energy gain due to redox reactions between the host \(\pi\)-conjugated polymer and the guest dopant, though structural factors, such as the unique size, conformation, and steric effect of molecular dopants in hybrid host–guest systems, may cause apparent limitations in the maximum achievable doping level\(^20,22\). However, such steric effects associated with the donor–acceptor association have not been investigated systematically in polymeric semiconductors because of the limited variations of host–guest systems.

In this work, we employ two distinct conjugated polymers with different alkyl side-chain densities, and characterize the doping efficiency regarding steric effects. Spectroscopic and magnetotransport measurements reveal that doping efficiency of polymers with sparse alkyl side-chains is significantly greater than that with dense side-chains. Steric effects between the \(\pi\)-conjugated semiconducting polymer and dopants could influence the donor–acceptor formation, which strongly limits the maximum achievable doping level in polymeric semiconductors. A closest-packed supramolecule is realized with a particular combination of a sparse polymer and a large dopant, giving rise to high conductivity, air stability, and remarkably high work function.

**Results and discussion**

**Difference in doping efficiency due to steric effects.** We focus on two distinct \(\pi\)-conjugated polymers, based on PNDTBT (poly(2,7-bis(3-alkylthiophen-2-yl)naphtho[1,2-b:5,6-b]dithiophene; Fig. 1a, b)\(^23-26\). PNDTBT is a series of naphthodithiophene–bithiophene polymers that shows an excellent field-effect mobility up to \(1\ \text{cm}^{2}\ \text{V}^{-1}\ \text{s}^{-1}\) due to its promoted, two-dimensional lamellar structure\(^24\). Specifically, two PNDTBT polymers with different alkyl side-chain densities are employed, PNDTBT-C20, with a sparse density, and PNDTBT-4C16, with a high density. PNDTBT-4C16 possesses four alkyl side-chains in a repeat unit, which clearly limits the size of the void space between each lamella. Space-filling, van der Waals-based representations of PNDTBT-C20 and PNDTBT-4C16 are shown in Figs. 1c, d. The characteristic void distance \(d_{\text{void}}\) is defined as the distance of the van der Waals surfaces between alkyl side-chains (Fig. 1c, d).

The molecular doping was performed via anion exchange\(^18\). In the anion-exchange doping, a solid-state thin film of PNDTBT was immersed in a dopant solution. Here, F\(_4\)TCNQ and lithiumbis(trifluoromethylsulfonyl)imide ([Li\(^+\)TFSI\(^-\)]) salt were co-dissolved in n-butyl acetate (see experimental details in the “Methods” section and Supplementary Information Section 1.1). The molecular doping proceeds with an initiator molecule F\(_4\)TCNQ possibly via a charge transfer reaction. The F\(_4\)TCNQ radical anions, which are part of the solid-state, donor–acceptor pairs [PNDTBT\(^{+}\)+F\(_4\)TCNQ\(^{-}\)], are then replaced instantaneously by TFSI\(^-\) via anion exchange (Fig. 1e)\(^18\). Anion-exchange doping allows both efficient molecular doping with an anion-exchange efficiency close to 100% and a wider variation of functional dopants to be incorporated into polymeric semiconductors. The molecular doping is efficient because the donor–acceptor association minimizes the Gibbs free energy, where the energy gain to form the donor–acceptor pair is believed to be governed predominantly by the redox potential, described by Marcus theory\(^27\). The anion exchange process utilizes an ionic interaction as an additional driving force in doping; an additional energy gain is expected due to a secondary donor–acceptor association via an anion exchange. Consequently, remarkably high doping levels, close to the half-filled state, can be achieved.

We characterize the doping efficiency with regard to the steric effects related to the unique void space of dopant anions in these two PNDTBT polymers. In the previous literature\(^24\), it was concluded that both polymers have an extended, planar conformation, which has been verified by X-ray diffraction (XRD), optical absorption measurements, and density functional theory (DFT) calculation. The backbone coplanarity and ordering for the PNDTBT-4C16 is slightly enhanced compared to the PNDTBT-C20. This is presumably because the additional alkyl groups on the naphthodithiophene core can fill the space between the alkyl groups on the thiophene rings which sandwich the naphthodithiophene core. Schematic illustrations of the lamellar structure of PNDTBT polymers are shown in Fig. 2a, b, where the red dotted squares denote the alkyl side-chain regions. We also performed DFT calculations to illustrate the van der Waals surfaces (Fig. 2c–f). Initially, the conformation of a monomer unit...
of PNDTBT with propyl side chains was simulated by DFT calculations. This monomer unit was then aligned along the π-stack direction with each polymer long axis being pushed aside by 3.7 Å. This value has been used typically for thiophene-based, crystalline polymers. In addition, the highest occupied molecular orbital levels for the two PNDTBT polymers are identical, determined by the observation of identical ionization potentials for both polymers (see Supplementary Information Section 1.2). This means that both polymers should undergo very similar redox reactions during molecular doping apart from their steric effects.

To assess the doping efficiency with regard to the steric effects, comparisons of the electronic and structural properties were investigated comprehensively between PNDTBT-C20 and PNDTBT-4C16. The optical absorption spectra reveal that a neutral π* absorption of PNDTBT polymers centered at approximately 500 nm is bleached, and a broad absorption at the near-infrared regime is observed after anion-exchange doping (Fig. 3a, b), which is consistent with hole doping of polymers. The broad absorption, which emerges after doping, may originate from localized polarons. A characteristic doublet originating from the F4TCNQ radical anion is not seen in the absorption spectra of thin films after anion exchange. The absence of F4TCNQ** after anion exchange is further verified by Fourier transform infrared (FTIR) spectroscopy (Fig. 3c, d). The FTIR spectra of the anion-exchanged thin films do not show the peak assigned to the C≡N stretching mode of the F4TCNQ** (2190 cm⁻¹), which is an indicative of efficient anion exchange (F4TCNQ** → TFSI⁻). Note that the FTIR spectroscopy may possibly identify the intermediate (either integer charge transfer state or charge transfer complex). Because no apparent superposition of neutral and anionized F4TCNQ peaks is observed in FTIR signal for polymers doped merely with F4TCNQ, it can be inferred that the intermediate during anion exchange is likely to undergo integer charge transfer. However, in reality, the initiator F4TCNQ and the second anion TFSI are supplied in solution at the same time, and the first initiation and second anion exchange processes may proceed cooperatively. Clearly, further studies are needed to identify the intermediate. The conductivity of thin films after anion exchange was increased by a factor of 4 and 40 compared with doping solely with F4TCNQ (see the conductivity values in the inset of Fig. 3a, b), suggesting that the doping level was improved by the efficient anion exchange with the optimum salt [Li⁺TFSI⁻].

The degree of hole doping is significantly different in terms of the alkyl side-chain density; the bleaching of neutral absorption and increase of broad absorption at the near-infrared regime are found to be significantly greater for PNDTBT-C20, suggesting that a higher doping level can be realized for PNDTBT-C20 than for PNDTBT-4C16. Note that the oscillator strength in two polymers is almost comparable because the conjugated core as well as its conformation for two polymers is found to be very similar. This trend is consistent with the experimentally measured electrical conductivity (σ = 183 S cm⁻¹ for PNDTBT-C20 and σ = 0.4 S cm⁻¹ for PNDTBT-4C16 after anion-exchange doping).
To address this difference, we investigated the host–guest hybrid structure by XRD measurements. The out-of-plane and in-plane XRD profiles of a pristine (black) and a doped (colored) PNDTBT thin film are shown in Fig. 3e–h. The first-order (100) diffractions against the scattering vector $q_z$ are clearly observed for the pristine PNDTBT thin films regardless of side-chain density (Fig. 3e, f), indicating that a two-dimensional, lamellar structure is established for both pristine PNDTBT thin films. The observation of a well-ordered lamellar structure of PNDTBT polymers is consistent with previous literature. The $d$-spacing is determined to be 23.4 Å for PNDTBT-C20. This $d$-spacing is clearly shorter than the length of all-trans alkyl chain of C20 (~26 Å), which suggests the possible side-chain inter-digitation. The densely packed alkyl group has an effective diameter of about 5 Å, which is much shorter than the distance of the van der Waals surface between the alkyl side chains ($d_{void}$) for the sparse PNDTBT-C20 (shown in Fig. 1c). On the other hand, $d_{void}$ for the dense PNDTBT-4C16 is about 4.5 Å (shown in Fig. 1d), and is notably shorter than the effective diameter of the alkyl group. This indicates almost no side-chain inter-digitiation for PNDTBT-4C16, which is consistent with the theoretical prediction. A larger $d$-spacing obtained for PNDTBT-4C16 (30.2 Å) is attributed to steric hindrance due to dense alkyl side-chains. We experimentally observe that the (100) diffractions are shifted in the small scattering vector direction for both PNDTBT thin films, which corresponds to an expansion of $d$-spacing. An 11% $d$-spacing expansion is obtained for doped PNDTBT-C20, whereas only a 4% expansion is obtained for doped PNDTBT-4C16. The changes in the in-plane diffractions along $q_{xy}$ after doping also show different behaviors between PNDTBT-C20 and PNDTBT-4C16; the π-stacking distance, derived from the (010) diffraction peaks, decreases by 3% for doped PNDTBT-C20, whereas the (010) diffraction for doped PNDTBT-4C16 is hardly observable, or comparable to the noise level of the measurements. The overall XRD results suggest that TFSI$^-$ dopants introduced by anion exchange can intercalate into a restricted void space, namely the limited alkyl side-chain zone of PNDTBT polymers. The spatially confined intercalation causes the $d$-spacing.
expansion, which is consistent with the previous literature. Because the void space formed between lamellae for PNDTBT-C20 is clearly larger than that for PNDTBT-4C16, a large d-spacing expansion is expected for PNDTBT-C20, which agrees with the experimental results. Note that a decrease of the π-stack distance observed for PNDTBT-C20 can be attributed to a suppression of torsion of the PNDTBT backbone by doping.

The steric selectivity found specifically in doped PNDTBT polymers is qualitatively understood by examining how TFSI is incorporated into the alkyl side-chain regime. It is found that PNDTBT-C20 can accommodate TFSI in its sparse alkyl side-chain zones without apparent short contact, whereas the incorporation of TFSI can be limited by short contacts between the dense alkyl side-chains of PNDTBT-4C16 and TFSI. Given that the molecular long axis of TFSI (d_{long}^{TFSI}) is much greater than the void distance of the alkyl side-chains of PNDTBT-4C16 (d_{void}^{TFPB} = 7.5 Å > d_{void} = 4.5 Å), the short contact displayed in Fig. 2d may be unavoidable. In a previous study, we verified that anion exchange takes place spontaneously as long as the secondary donor–acceptor association reduces the Gibbs free energy. This situation can be achieved when the secondary donor–acceptor association has the optimum conformation. However, efficient anion exchange is no longer expected due to the presence of steric hindrance between alkyl side-chains of PNDTBT-4C16 and dopants, which limits the dopant incorporation and doping levels.

Formation of closest-packed supramolecules. From the observations above, we presume that PNDTBT-C20 is capable of accommodating a wider variety of functional anion dopants than has previously been considered. Particularly in the anion exchange process, the formation of an ion pair between a polymer and a large anion is likely to produce a large energy gain. This trend is intuitively understood by considering the empirical hard and soft acids and bases theory, which has been often invoked to explain ion exchange phenomena. To verify the concept, we selected another anion tetrakis(pentafluorophenyl)borate (TFPB, shown in Fig. 4a, b). For DFT calculations, the molecular long axis of TFPB is estimated to be 11.5 Å, and its electrostatic potential is found to be delocalized. This is because the electrostatic potential might be blurred due to the spread of the charge density to the phenyl group and the electron-withdrawing fluorne substituent. Anion-exchange doping with TFPB was performed with a mixed dopant solution (F4TCNQ and [Li^+TFPB^-] ethyl ether salt co-dissolved in 1,2-dichloroethane). As expected, efficient anion-exchange doping was verified by observing the bleaching of the neutral absorption of PNDTBT-C20 (Fig. 4c) and absence of F4TCNQ in FTIR spectra (the inset of Fig. 4c). The electrical conductivity obtained for PNDTBT-C20 with TFPB is increased by a factor of 2.5 compared with that with TFSI-. In addition, the incorporation of bulky TFPB- is further confirmed by out-of-plane XRD measurements (Fig. 4d); the characteristic d-spacing is expanded by
were calculated using DFT with the B3LYP functional and 6-31+G(d) basis set (Spartan’16 software). These calculated electrostatic potentials are based on the van der Waals surfaces of the anions. The spatial distributions of the electrostatic potentials were visualized by electrostatic potential maps (Fig. 4e, f). The obtained electrostatic potential maps show that even the bulky TFPB anion-exchange doped with TFPB− (green) should not improve the doping levels because there is likely to be a short contact between alkyl side-chains of PBDTT and TFPB, which can facilitate the accommodation of a wide variety of functional dopants, and such controlled steric selectivity may be a key for developing further improvements of molecular doping.

The increase in conductivity for the bulky anion TFPB− was further investigated by magnetotransport measurements. The Hall effect is a powerful tool for determining charge carrier density and mobility separately, and also for assessing whether charge carriers undergo coherent, band transport, because the Hall voltage is only observed when the charge carriers undergo a free-electron-like transport. We observed a clear transverse (Hall) voltage using a Hall bar geometry (Fig. 5a, see more details in Supplementary Information Section 1.2). The symmetry and sign of the voltage correspond to the hole carrier conduction. From the obtained Hall voltage, the Hall carrier density \( n_H \) can be derived from the inverse Hall coefficient \( n_H = (eR_H)^{-1} \), and the Hall mobility \( \mu_H \) can be determined from \( \mu_H = R_H \). Comparisons of \( n_H \) and \( \mu_H \) between PNDTBT-C20 thin films and TFPB− are summarized in Fig. 5b, c. The doping density (hole per monomer unit) was estimated from the Hall carrier density and unit monomer density. In the previous literature, the unit cell volume of PNDTBT polymer was determined to be \( 1.49 \times 10^{-21} \) cm−3, equivalently monomer density of \( 6.71 \times 10^{-20} \) cm−3. With the experimentally determined Hall carrier density of \( 6.8 \times 10^{20} \) cm−3, the doping density is estimated to be 1.0 and 1.3 hole per monomer unit for PNDTBT-C20 with TFSI− and with TFPB−, respectively. The results showed that the increased conductivity with TFPB− can be attributed to both the increased Hall carrier density and Hall mobility. The latter originates clearly from the improved crystallinity shown in Fig. 4d. A remarkably high carrier density corresponding to one hole per monomer unit achieved for PNDTBT-C20/TFPB− is further confirmed by photoelectron yield spectroscopy. Figure 5d plots the photoemission yield as a function of the incident photon energy, from which the ionization potential, equivalent to the effective Fermi energy, is monitored. We observed a larger shift in the threshold photon energy for PNDTBT-C20 with TFPB−. This suggests that the formation of the ion pairs [PNDTBT-C20+ + TFPB−] produces a
The error bars in the conductivity show the uncertainty in the thickness of the polymer thin films, and represent one standard deviation. The Hall voltage was not detectable for the pristine PNDTBT-C20 because the sample was highly resistive (the largest gain of Gibbs free energy compared to the pairs [PNDTBT-4C16]− and [PNDTBT-C20]−). DFT calculations were conducted to visualize the van der Waals interaction between the monomer structure and the dopant anions. Initially, the conformation of a particular combination of a sparse conjugated polymer and an extraordinarily large dopant anion, which gives rise to high conductivity, high air stability, and a remarkably high work function. This work provides a critical insight into how to overcome steric effects in molecular doping, and highlights the importance of molecular engineering for further improvements of doping efficiency.

**Methods**

**Materials.** A family of naphthodithiophene–biophiophene polymers with different alkyl side-chain densities, namely PNDTBT-C20 with a sparse density and PNDTBT-4C16 with a high density, were synthesized and purified in house. The molecular weight $M_n$ and polydispersity index (PDI) were estimated to be 59.95 kDa and 1.46 for PNDTBT-C20 and 47.8 kDa and 1.76 for PNDTBT-4C16 (see more details in Supplementary Information Section 1.1). Polymer thin films were deposited via spin-coating from chloroform solutions. Anion-exchange doping was performed by immersing solid-state thin films into dopant solutions at 60°C for 10 min in N$_2$-purged vials. The concentration of dopants and the employed solvents are listed in Supplementary Table S1. After being removed from the vial, the films were annealed at 80°C for 10 min, and the residual solvent was blown off under a flow of N$_2$.

**Transport measurements.** Conductivity data were collected with a two-terminal device configuration. Doped polymer thin films were deposited onto Cr (3 nm) and Au (30 nm) electrodes, and then patterned into a rectangular shape to avoid the fringe effect that causes an overestimation of conductivity. For conductivity measurements, three devices with different channel lengths were tested. Hall effect measurements were performed using a Hall bar geometry, where the doped PNDTBT thin film was patterned by dry etching to allow precise measurements of the local potentials of probes along a channel. Cr (3 nm) and Au (30 nm) electrodes were thermally evaporated through a shadow mask on a pre-cleaned glass substrate. The PNDTBT thin film was deposited in a similar manner, and then patterned into the Hall bar geometry by laser etching using an yttrium aluminum garnet laser. Hall effect measurements were performed using an He gas exchanged cryostat with a superconducting magnet. Both the longitudinal and transverse electromotive forces were monitored simultaneously while applying a dc current of 1 μA and sweeping the magnetic field from 0 to −10 T at a rate of 0.4 T min$^{-1}$.

**DFT calculations.** DFT calculations were conducted to visualize the van der Waals surface of PNDTBT monomer and dopant anions. Initially, the conformation of a monomer unit of polymers with propyl side-chains was simulated through structural optimization by DFT calculations, i.e., the monomer structure was energetically minimized (using the B3LYP functional and 6-31+G(d) basis set). Note that the conformation of alkyl side chains impacts on steric selectivity, but it is known from the literature that alkyl side chains attached thiophene unit are likely to form all-trans conformation. Thus, replacing long side chains with the propyl group might be reasonable for qualitatively understanding steric effects in the present system. To construct a realistic molecular assembly of polymers, this monomer unit was then aligned along the π-stacking direction with each polymer long.
axis being pushed aside by 3.7 Å. This value has been used typically for thiophene-based, crystalline polymers. Finally, dopant anions were placed close to void spaces merely for visualizing whether the polymers’ void space can accommodate dopant anions without short contact.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author (S.W.; swatanabe@edu.k.u-tokyo.ac.jp) upon reasonable request.

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