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Supramolecular cocrystals built through redox-triggered ion intercalation in π -conjugated polymers

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Self-organization in π -conjugated polymers gives rise to a highly ordered lamellar structure, in which inter-chain stacking spontaneously forms two-dimensional conjugated sheets. This multi-layer stacked nature of semicrystalline polymers results not only in effective charge transport, but also allows the inclusion of various functional molecules and ions. In particular, redox-triggered ion-intercalation in a polymer's lamellae is an ideal system for molecular doping, for which extremely high charge carrier density, corresponding to one carrier per monomer unit, has been achieved. We conducted a detailed structural analysis and electron density simulation to pinpoint exactly where the guest dopants are located periodically in the restricted void space in a polymer's lamellae. Our findings are indicative of an intercalation compound of layered polymers and a guest intercalant. In addition, we show that a homogeneous cocrystal structure can be realized throughout the host polymer medium, which is proved unambiguously by the observation of coherent carrier transport across microscopic-scale films. Also, the intercalation cocrystal nature gives the best achievable doping level in semicrystalline conjugated polymers and excellent environmental stability. These findings should open up new possibilities for tuning the collective dynamics of functional molecules and ions through intercalation phenomena.

Doping of semiconductor materials is an essential technology common to any electronic devices, by which the charge carrier density can be tuned by several orders of magnitude, allowing precise control of the Fermi energy in electronic systems.^{1,2} For the inorganic semiconductor Si, for example, impurity doping is achieved by substituting Si atoms in a periodic crystal with an electron-accepting or electron-donating element. The original, periodic crystal structure of the Si can be maintained even after the implantation of impurity dopants.^{2,3} In organic semiconductors (OSCs), on the other hand, the fundamental doping process can be very different. This is because the doping agents for OSCs are not atoms, but are molecules having a unique size and conformation. Molecular doping via redox reactions between the host OSC and a guest dopant has been studied extensively in material sciences, chemistry, and physical engineering.⁴⁻¹² It remains a challenge to achieve extremely high doping levels, though heavily doped polymers have been produced via self-compensation by covalently bounded counter-ions¹³⁻¹⁵ and photo-doping.¹⁶

Recently, relatively high doping levels (nearly one charge per monomer unit of a π -conjugated polymer, *i.e.*, a half-filled state) have been achieved via solid state diffusion¹⁷⁻²⁰ or anion exchange,^{21,22} where molecular dopants are introduced sequentially in the pre-deposited thin film of semicrystalline polymers. To achieve extremely high doping levels via molecular engineering, the molecular dopant must be inserted selectively into void spaces in semicrystalline π -conjugated polymers,^{17-20,23} where alkyl side-chains would normally be located, *i.e.*, between the polymer’s lamellae. Hence, the inclusion of dopant molecules is severely limited, not only by the original crystal structure of OSCs, but also by the structural admixture between the host OSC and guest dopants.⁷⁻¹⁰ Although this may impose an apparent limitation on the maximum achievable doping level in OSCs, it is controversial how a “soft lattice” in semicrystalline polymers can be susceptible to dopant molecules, and to what extent the delicate balance in the structural admixture can be maintained.

In this study, we consider redox active radical salts as an acceptor dopant. A standard polythiophene-based, semicrystalline polymer can be doped efficiently with radical salts, resulting in remarkably high doping levels. Importantly, we perform detailed structural analysis and electron density simulations and show that the position of a guest anion inserted into a polymer’s lamellae is confined spatially in the restricted void in each lamella; in other words, layered π -conjugated polymers and intercalant anions can cooperatively build a supramolecular cocrystal. We demonstrate the best possible doping level for the closest

packing structure, which is estimated to be exactly one-electron per monomer unit. This finding will help us understand coherent carrier transport in this system, and enable the design of interaction phenomena between the host and guest through molecular engineering.

We focus on donor–acceptor systems composed of a p-type polymeric semiconductor, poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT), and functional dopants. PBTTT is a widely studied, semicrystalline polymer, which spontaneously develops a two-dimensional lamellar structure from a solution process (Fig. 1a).^{24–27} To accomplish p-type molecular doping, a solid-state thin film of PBTTT is immersed in a dopant-dissolved solution (see detailed doping methods in Supplementary Information 1.1). Here, four types of acceptor dopants are investigated: 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), molybdenum tris(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) (Mo(tfd-COCF₃)₃),²⁸ Li-bis(trifluoromethylsulfonyl)imide (Li-TFSI via anion exchange route), and tris(4-bromophenyl)ammoniumyl bis(trifluoromethylsulfonyl)imide (TPA-TFSI). Molecular structures and electrostatic potential maps are shown in Fig. 1b, and the energy alignment of the redox potentials is shown in Fig. 1c. TPA is a family of nitrogen centered radical cations, which has been investigated as strong oxidants that can externally generate radical cations.^{29,30} Among them, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TPA-SbCl₆), termed “magic blue”, is recognized by chemists for having a strong oxidation ability and simple electron transfer reactions. In general, the oxidation ability and stability of TPA salts can be readily tuned by aryl substituents and counter-anions.³⁰ We selected the TFSI anion for its size and hydrophobicity, which brings high stability, and for the good electrical performance of the doped polymer, which was revealed in our previous anion exchange doping study.²¹

Ultraviolet-visible near-infrared (UV-vis-NIR) spectroscopy confirms that a neutral absorption of PBTTT centered at 553 nm is bleached and a broad absorption in NIR region emerges (Fig. 1d), which is consistent with p-type doping of the polymer via redox reaction with acceptor dopants.^{17–19} By comparing the conventional dopants F4TCNQ and Mo(tfd-COCF₃)₃, bleaching of neutral absorption and an increase in the broad absorption in the NIR region occur for anion-exchange doping and TPA-TFSI doping, suggesting that a higher doping level can be realized for anion-exchange and TPA-TFSI doping. Particularly, in the doping process with a TPA radical salt, the TPA radical cation is responsible for an initial one-electron transfer, mainly due to the half-cell reaction: $\text{TPA}^{\bullet+} + \text{e}^- \rightarrow \text{TPA}$. This con-

verts the TPA radical cation to a neutral state, while leaving the TFSI⁻ as a counter-anion to guarantee charge neutrality with respect to the positively charged polymer. Note that the residual, neutral TPA, is not present on the surface of PBTTT thin films because it dissolves well in acetonitrile.

The doping level of PBTTT thin films was further evaluated by electrical conductivity measurements and photoelectron yield spectroscopy (PYS) (see detailed information in Supplementary Information 1.2). The conductivity of a PBTTT thin film doped by anion exchange and with TPA-TFSI increased significantly by a factor of approximately 3 compared with doping solely with F4TCNQ or Mo(tfd-COCF₃)₃ (Fig. 1e), which is consistent with the optical absorption measurements. In addition, PYS measurements allow us to monitor the degree of doping; the ionization potential that corresponds to the work function (Φ_{eff}) was evaluated from the energy threshold of the photoemission yield, Y (Fig. 1f, and Supplementary Information 1.2). The Φ_{eff} for a pristine PBTTT thin film was measured to be 4.8 eV, which is close to the literature value of the highest occupied molecular orbital (HOMO).^{24–27} A positive shift in the Φ_{eff} for the doped films is clearly observed as the doping level increases, and the largest shift is observed for PBTTT doped with TPA-TFSI. These shifts agree with p-type doping of PBTTT, where electrons are removed from the HOMO band.²¹ The Φ_{eff} values are evaluated to be 5.2 eV for F4TCNQ doping, 5.4 eV for Mo(tfd-COCF₃)₃ doping, 5.4 eV for anion-exchange doping, and 5.6 eV for TPA-TFSI doping, which roughly agree with the estimated redox potentials of the dopants (Fig. 1c).^{10,28} We emphasize that a Φ_{eff} of 5.6 eV is even larger than that achieved for anion exchange doping.²¹ The overall results suggest that the donor–acceptor system tries to minimize the Gibbs free energy via a charge transfer interaction; electrons within the HOMO band of the polymer are transferred to the level of the redox potential (electron affinity) of the dopants, such that Φ_{eff} is close to the redox potential of the dopant, and the resulting donor–acceptor formation minimizes the Gibbs free energy at equilibrium such that no further charge transfer occurs. Clearly, the strong oxidation capability of the TPA radical cation is advantageous for improving the doping levels of the polymer.

This observation of remarkably high doping levels indicates that TFSI anions are incorporated into the polymer, such that they are in counter-balance to the positively charged PBTTT, which raises the question regarding where such high-density anions, equivalent to the amount of PBTTT monomers, can reside within the semicrystalline polymer net-

work. To assess this, we performed X-ray diffraction (XRD) measurements and an electron density analysis. Out-of-plane and in-plane XRD profiles for pristine (black), F4TCNQ-doped (blue), and TPA-TFSI doped PBTTT (red) thin films are shown in Figs. 2a and b. Typically, several orders of ($h00$) diffraction peaks, according to the lamellar spacing, are observed in the out-of-plane direction along the scattering vector q_z . The diffraction peaks for doped PBTTT are found to shift to shorter q_z , which corresponds to an expansion of the lamellar spacing.^{17,31–34} Surprisingly, a 20% d -spacing expansion is obtained for the TPA-TFSI doped PBTTT (d_{h00} shift in top panel of Fig. 2c). On the other hand, the in-plane diffraction along q_{xy} after doping shows different behavior; the diffraction peaks assigned to (003), corresponding to the periodicity of the monomer repeat unit, is insensitive to doping, and those assigned to (010), corresponding to the π -stacking direction, shift to a larger scattering vector direction as the doping level increases. These XRD results suggest that dopants reside selectively in the alkyl side chain regions (resulting in lamellar expansion), and do not distribute into planar polymer planes (π - π spacing). The decrease in d_{0k0} may be attributed to suppression of torsion in the PBTTT backbone upon doping²¹ or to ionic interactions between positively charged PBTTT and counter-anions.³⁵

Although spatial selectivity of dopant inclusion in the present semicrystalline polymer and dopant system has been observed,^{17,21} a critical difference is found in PBTTT highly doped with TPA-TFSI. Figure 2a shows the out-of-plane diffraction peaks ($h00$) for pristine and F4TCNQ doped PBTTT, exhibiting a monotonic decrease with increasing the Miller index ($h00$). In striking contrast, the (300) diffraction peak for TPA-TFSI doped PBTTT vanishes, with its intensity being comparable to the noise level of the measurements, while higher order diffraction peaks (400) and (500) are clearly observed. Typically in XRD measurements of semicrystalline polymers, higher order diffraction peaks diminish rapidly as the Miller index increases because the degree of structural disorder for a polymer can be much larger than that for a single crystal.^{25,36–40} Thereby, the missing (300) diffraction peak for the TPA-TFSI doped PBTTT might not be explained by established diffraction theory for paracrystalline materials used for disordered polymers.

Loss of diffraction intensity commonly occurs in single-crystal XRD due to selection rules. This is a consequence of destructive interference of scattered X-rays.⁴¹ The intensity of diffraction in a periodic system is proportional to the square of the absolute value of the structure factor, which can be derived from a Fourier transform and a convolution

of the electron density of a repeating motif. Thus, the electron density of a repeating motif determines whether the interference is constructive or destructive. In turn, analyzing higher-order diffraction intensities allows us to determine the periodic electronic structures of layered compounds.^{31,42} In order to examine the loss of the (300) peak and obtain a detailed electron density profile in doped PBTTT thin films, an XRD intensity simulation along the out-of-plane direction was conducted for pristine, TPA-TFSI, and TPA-SbCl₆ doped PBTTT. The degree of (300) loss is found to be different between SbCl₆ and TFSI anions, although both achieve similar doping levels.

In our simulation, the electron density profile for isolated, monomer PBTTT was initially obtained from density functional theory (DFT) calculations with the Gaussian 09 package, projected in the out-of-plane direction (z -axis). This was then used to produce the electron density profile of a z -axis periodic PBTTT lattice using the experimentally determined $d_{h00} = 21.4$ Å. Figure 3a shows the one-dimensional electron density $N(z)$ along the z -axis, where the electron density profile for the repeating motifs is shown separately for PBTTT backbones (orange) and alkyl chains (gray), and the total electron density profile, namely the sum of each motif, is shown as a solid curve. A Fourier transformation was applied to the electron density profile of the PBTTT lattice to obtain the structural factor. For doped PBTTT, the electron density profile for anions was added to that for the pristine PBTTT, where the periodic electron densities were reconstructed using the experimentally determined $d_{h00} = 26.7$ Å for TFSI and 24.9 Å for SbCl₆. Figures 3b and c show the electron density profile with TFSI (red) and SbCl₆ (purple). We introduce four variable parameters: z_{anion} , the weighted-center position of an anion relative to that of the polymer, ϕ_{alkyl} , the tilting angle of the alkyl chains relative to the out-of-plane direction, n_{anion} , the amount of anions per monomer of PBTTT, and σ , the degree of Gaussian disorder. These four variable parameters were estimated by the least squares method so that all the simulated intensities of the ($h00$) diffraction peaks match the experimental intensities. The detailed method is described in Supplementary Information 1.3.

Figures 3a–c show simulation results for electron density profiles that reproduce the ($h00$)-dependent XRD intensities. The agreement for the ($h00$)-dependent XRD intensities between experiments and simulation is shown in Fig. 3d. By optimizing the four variable parameters to achieve a global minimum of the fitting (see Table 1), a monotonic decay in the XRD intensities with respect to the Miller index due to structural disorder, and a

characteristic decrease of (300) intensities are reproduced. We do not detail the mechanism of the disappearance of the (300) peaks (a more detailed explanation is shown in Supplementary Information 1.4.), but we emphasize that a unique XRD profile such as in the present host-guest system, particularly for the observed destructive interference of XRD, can occur only when the intercalant is precisely located within the host lattice with the molecular precision preserved. Although there are four variable parameters in our simulation, the vital parameters determining the outcome of the experiments are found to be the position of the anions z_{anion} and the number of anions n_{anion} . These two parameters are determined explicitly to be $z_{\text{anion}} \sim 5 \text{ \AA}$ and $n_{\text{anion}} = 0.9\text{--}1.1$, meaning that the weighted-center position of the anions is exactly $5 \text{ \AA}$ away from the backbone of the PBTTT, and there is almost one anion paired with each PBTTT monomer unit. This agrees with the experimentally observed carrier concentration, as discussed later. To verify this, we performed X-ray photoemission spectroscopy (XPS) analysis. The elemental analysis for the elemental composition ratio of carbon to fluorine for TFSI-doped PBTTT shows that the TFSI content relative to PBTTT is 0.86 (Supplementary Information 1.5), which is consistent with the XRD simulation results.

The heterogeneous, layered system of semicrystalline conjugated polymer and guest molecule is analogous with an intercalation compound. Intercalation is a chemical process in which guest agents, atoms, molecules, or clusters are incorporated into the interlayer gallery space of layered hosts, eventually forming hybrid heterostructured materials. The host materials can be inorganic or organic, and their applications include batteries and electric and ionic conductors.^{43–45} In ionic intercalation compounds, a guest ion intercalates into an oppositely charged sheet of the host two-dimensional material, resulting in an expansion of the van der Waals gap. A charge transfer interaction, *i.e.*, a redox interaction, facilitates stabilization of the host and guest sheets. Such a controlled structure of the host and guest offers a platform for designing a system with desirable functionalities. Intercalation compounds based on graphite and the transition metal dichalcogenide have been widely studied,^{43–45} but intercalation phenomena are also found in organic materials such as small molecular conductors⁴⁶ and lipids.⁴⁷ However, there have been no previous reports on realizing intercalation compounds with a layered, semicrystalline polymer as the host platform, accommodating extremely high-density guest agents periodically.

In the hybrid host-guest system demonstrated here, the spatially confined guest anions

may give rise to unique electronic functionalities because these anions inserted periodically into the polymer medium are in counter-balance to the positively charged polymer. Measuring the Hall effect is a powerful way to determine the charge density and the Hall mobility, and to distinguish the nature of the carrier localization. The Hall voltage, that is the transverse electromotive force generated in a conductor when placed in a magnetic field perpendicular to the current, is measurable only when the coherent wave packet of a delocalized electron that can be described with a semiclassical Boltzmann transport framework experiences the magnetic field.^{17,21,22} In other words, charge carriers that undergo hopping transport never generate an ideal Hall voltage. Figure 4a shows the representative time domain profile for the transverse voltage at 240 K for TPA-TFSI doped PBTTT thin films. A clear Hall voltage responding to the applied magnetic field B is observed. From the standard expression of the Hall effect, the Hall mobility μ_H and the Hall carrier density n_H are determined and shown in Fig. 4b. A reasonably high n_H of approximately $1.5 \times 10^{21} \text{ cm}^{-3}$ is achieved, concomitant with a high μ_H of $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. 4b). This carrier density is identical to one hole per monomer unit or slightly greater. Importantly, the values for the charge carrier density derived separately from the Hall effect (Fig. 4b), electron density simulation (Table I) and XPS elemental analysis (Supplementary section 1.5) show almost perfect agreement, which strongly suggests that the proposed intercalation system with spatially confined guest anions is realized predominantly for the entire thin film. Note that the similar supramolecular cocrystal has been observed for the PBTTT/fullerene derivative system,³¹ where the amount of intercalant was found to be limited by unavoidable aggregation and phase separation. A critical factor that differentiates these supramolecular cocrystals is that the creation of doping-induced cocrystals can be initiated by redox-triggered ion-intercalation, which enables an ideal production of homogeneous cocrystals without phase separation or aggregation.

The spatial homogeneity of TPA-TFSI doping presented in this work is further assessed using a thick polymer film. A $5\text{-}\mu\text{m}$ -thick PBTTT film was deposited via a modified drop-casting method, and was immersed in a TPA-TFSI solution (see Supplementary Information 1.6 for experimental details). Figure 4c plots the out-of-plane XRD patterns for pristine and TPA-TFSI doped PBTTT thick films. Even for the $5\text{-}\mu\text{m}$ -thick film, the $(h00)$ diffraction peaks are found to shift to shorter q_z with no splitting or broadening of the full width at half maximum (FWHM) (Fig. 4d). In addition, reduction of the (300) diffraction intensity for

doped films was observed, similar to the doped thin films. The FWHM for the diffraction peaks decreases after doping, which demonstrates that the degree of cumulative disorder decreases by doping (Fig. 4d). Note that the X-ray penetration depth used here was estimated to be approximately 10 μm , and is larger than the film thickness, ensuring that the entire film was evaluated. These results suggest that TFSI anions are incorporated into the entire bulk of the 5- μm -thick PBTTT film, and the proposed intercalation supramolecular structure can be established. Details of the dopant dynamics still remain unknown. Considering that the chemical doping is mainly driven by the redox potential difference, which is on the order of sub-electronvolts, and is far higher than the thermal energy, spontaneous bulk doping can be a consequence of the host-guest system minimizing the Gibbs free energy. We note that various factors,⁴⁸ such as size, solvation of the dopant anion, softness of the polymer lattice, and void space in the polymer film, play important roles, and will be assessed in the future.

The inclusion of functional anions into layered media is known to change the physicochemical properties.^{32,34,43–45} Surprisingly, we found that the environmental durability of the doping effect depends strongly on the incorporated functional anions. We investigated the changes in the doping effect for TPA-X ($X = \text{PF}_6$, SbCl_6 , and TFSI) doped thin films by optical absorption and conductivity measurements. The effect of doping for PF_6 and SbCl_6 doped PBTTT was found to decrease rapidly after 88 hours storage in ambient conditions of 22°C and 40% relative humidity. The bleached optical absorption of the doped films returned to the neutral state (Figs. 5a and b) and the conductivity decreased by several orders of magnitude (Fig. 5c). For TFSI-doped PBTTT, changes in the optical absorption spectra seem to be largely suppressed and the degradation of the conductivity is much slower. It is reasonable to envisage that the doping effect of anions can be quenched by unintentional H_2O adsorption by exposure to ambient air. We therefore speculate that the H_2O molecule adsorption rate may correlate with the intercalation structure, and depend on the incorporated anions. For TFSI-doped PBTTT, the number of H_2O molecules that diffuse through the polymer void and are chemisorbed at the surface of TFSI anions may decrease significantly. Figures 5d–f illustrate DFT simulation results for the surface electrostatic potential and their space filling in the present systems with one anion per monomer unit (see more details in Supplementary Information 1.7). For the TFSI anions, a strong, albeit local, surface electrostatic potential was obtained, particularly at the single nitro-

gen and four oxygen sites, which is comparably strong as the PF_6 anions. In general, a large electrostatic potential on a molecular surface is likely to produce strong electrostatic interactions and water adsorption⁴⁹; thus, intuitively the best stability will be found for SbCl_6 -doped PBTTT. However, SbCl_6 -doped PBTTT shows poor stability, as comparable as PF_6 -doped PBTTT. Instead, TFSI-doped PBTTT shows the best stability. We speculate that this non-intuitive result originates from the unique conformation of TFSI anions relative to the polymer backbone; the nitrogen and two of the four oxygen sites in the TFSI anions that should interact strongly with the H_2O molecules are sterically protected by the polymer backbone, and become inaccessible to H_2O molecules (Fig. 5e). Furthermore, the intercalation compound TFSI-doped PBTTT may approach a closest-packed structure, for which the filling of the void space between each lamellae may help to reduce the accessible surface for H_2O molecules. The effects of void filling reducing the accessible surface area has been investigated for amorphous polymers, for which a molecular additive in the void in amorphous polymers has been found to improve device stability significantly.⁵⁰ Therefore, supramolecular engineering to form intercalation compounds that can potentially confine the position and conformation of reactive sites of functional anions may lead to further improvements of the physicochemical properties.

In this study, we have demonstrated doping of polymeric semiconductors with radical salts, where radical cations with strong redox activity are responsible for electron transfer. Our observations show that at the extremely high doping levels achieved by the present doping method, a soft lattice of semicrystalline polymers maintains its molecular precision by the periodic inclusion of dopant anions, for which the position and conformation of the guest dopant can be confined spatially in the restricted void space in the polymer’s lamellae. Realizing closest-packed intercalation supramolecules leads to the best attainable doping level in semicrystalline conjugated polymers and excellent environmental stability due to the limited accessible surface. These findings should therefore shed light on possibilities for the storage, transport, and conversion of functional molecules and ions through intercalation phenomena, and the construction of novel host–guest systems of crystalline doped polymers to achieve desirable optoelectronic properties.

Methods

The data supporting the findings of this study are available within this paper and the Supporting Information.

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Author contributions

T.O., Y.Y., and S. W. conceived the proof-of-concept of the doping method. Y.Y., K.U., J. Tsurumi, Y.T., S. Kohno, and S.W., designed and performed the experiments and analyzed the data. T.K., H.K., and S. Kumagai, synthesized the series of TPA dopants. S.W., Y.Y., and T.K., wrote the manuscript. S.W. and J. Takeya, supervised the work. All authors discussed the results and reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Data availability and corresponding author

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

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Table I: Results of fitting.

Dopant	z_{anion} (Å)	ϕ_{alkyl} (°)	n_{anion} (monomer ⁻¹)	σ (Å)
None (pristine)	–	27	0	2.2 ± 0.3
TFSI	5.1 ± 0.3	20 ± 11	0.91 ± 0.03	1.9 ± 0.2
SbCl ₆	5.0 ± 0.7	36 ± 16	1.09 ± 0.15	1.6 ± 0.6

Figure 1: Comparison of chemically doped PBTTT thin films with conventional and newly developed dopants. **a.** Illustration of chemical doping of a PBTTT thin film. **b.** Chemical structures of employed dopants and **c.** their reported redox potentials accompanied with the approximate valence band top of PBTTT. **d.** UV-Vis-NIR spectra, **e.** conductivities, and **f** photoelectron yield spectroscopy measurements for pristine (black), F4TCNQ (blue), Mo(tfd-COCF₃)₃ (green), Li-TFSI via anion-exchange (orange), and TPA-TFSI (red) doped PBTTT thin films. The error bars in the conductivities represent the uncertainty in the thickness of the PBTTT thin films and represent one standard deviation.

Figure 2: Out-of-plane and in-plane XRD measurements of chemically doped PBTTT thin films. **a.** Out-of-plane XRD measurements of chemically doped PBTTT thin films. The peak marked with an asterisk is attributed to aggregated F4TCNQ on the surface of the thin film. **b.** In-plane XRD measurements of chemically doped PBTTT thin films. The peaks with the square markers are mainly attributed to the periodicity of the PBTTT backbone in the main chain direction, while the peaks with the triangle markers arise from the periodicity of π stacking of the PBTTT. **c.** d -spacings extracted from XRD measurements, where d_{h00} corresponds to stacking of PBTTT sheet structures in the out-of-plane direction, d_{00l} corresponds to the length of the repeating unit of the PBTTT backbone, and d_{0k0} corresponds to the π stacking distance in the in-plane direction. The error bars for the d -spacings were determined from uncertainties in the fitting and represent one standard deviation.

Figure 3: Simulation of XRD peaks and structures of doped PBTTT. Models of **a.** pristine PBTTT, **b.** PBTTT doped with TFSI anion, and **c.** PBTTT doped with SbCl₆ anion, obtained from our simulations. The models are shown as side views, where the left axis represents the position in the out-of-plane direction. Left panels: Electron density profiles, $N(z)$, for the repeating motifs for the PBTTT backbone (orange), alkyl chains (grey), TFSI anions (red), and SbCl₆ anions (purple). Middle panels: Electron density profiles, $N(z)$, for the repeating motifs integrated for all the components. Right panels: Side views of the modeled PBTTT and chemically doped PBTTT obtained from our simulations. **d.** Comparison of experimentally obtained and simulated intensities of ($h00$) diffraction peaks for pristine and chemically doped PBTTT thin films. The error bars in the experimentally obtained peak intensities were determined from uncertainties in the Gaussian fitting of spectra and represent one standard deviation.

Figure 4: Hall effect measurements and homogeneity of doping effect. **a.** Hall voltages and the applied magnetic field B in the out-of-plane direction and **b.** Hall carrier density n_{H} derived from the inverse Hall coefficient $n_{\text{H}} = (eR_{\text{H}})^{-1}$ and Hall mobility μ_{H} estimated from $\mu_{\text{H}} = R_{\text{H}}\sigma$ for PBTTT thin films doped with F4TCNQ (blue), Mo(tfd-COCF₃)₃ (green), anion-exchange (orange), and TPA-TFSI (red) at 240 K. The error bars in n_{H} and μ_{H} represent uncertainties in extracting the Hall voltage from the fitting and the thickness of the polymer thin films and represent one standard deviation. **c.** Out-of-plane XRD measurements of a PBTTT film with a thickness of 5 μm before and after TPA-TFSI doping. **d** Miller index dependence of FWHM for pristine and TPA-TFSI doped PBTTT thick film.

Figure 5: Ambient stability of doped PBTTT. UV-Vis-NIR spectra for a pristine (gray), TPA-PF₆ (light blue), TPA-SbCl₆ (purple), and TPA-TFSI (red) doped PBTTT thin films. Data were acquired **a.** as doped and **b.** after 88 hours air exposure. **c.** Ambient stability of conductivities of TPA-PF₆ (light blue), TPA-SbCl₆ (purple), and TPA-TFSI (red) doped PBTTT thin films. Electrostatic potential map on molecular surfaces for ion pairs of **d.** PBTTT/PF₆, **e.** PBTTT/SbCl₆, and **f.** PBTTT/TFSI, together with their space-filling, van der Waals-based representation. The calculations of these potentials were conducted with Spartan'16 software with the M06-2X functional and 6-31++G(d,p) basis set, where a pseudopotential is applied to the Sb atom.

Figures

Figure 1

Comparison of chemically doped PBTTT thin films with conventional and newly developed dopants. a. Illustration of chemical doping of a PBTTT thin film. b. Chemical structures of employed dopants and c. their reported redox potentials accompanied with the approximate valence band top of PBTTT. d. UV-Vis-NIR spectra, e. conductivities, and f photoelectron yield spectroscopy measurements for pristine (black), F4TCNQ (blue), $\text{Mo}(\text{tfd-COCF}_3)_3$ (green), Li-TFSI via anion-exchange (orange), and TPA-TFSI (red) doped PBTTT thin films. The error bars in the conductivities represent the uncertainty in the thickness of the PBTTT thin films and represent one standard deviation.

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