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Efficient molecular doping of polymeric semiconductors driven by anion exchange

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Supplementary Materials for
Efficient molecular doping of polymeric semiconductors driven by anion
exchange

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1. Supplementary methods and discussion

1.1 Materials

The polymeric semiconductor poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT-C14) is one of the most widely studied p-type semiconductors, and is known to exhibit high field-effect mobility. PBTTT with an estimated molecular weight of 40,000 to 80,000 was purchased from Sigma-Aldrich and used as received. *o*-dichlorobenzene (*o*DCB) for use as a solvent for PBTTT was purchased from the FUJIFILM Wako Pure Chemical Corporation (Wako), while the acceptor dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4TCNQ) was purchased from Tokyo Chemical Industry (TCI). The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI), 1-butyl-3-methylimidazolium TFSI (BMIM-TFSI), 1-methyl-1-propylpyrrolidinium TFSI (MPPyrr-TFSI), 1-butylpyridinium TFSI (BPyri-TFSI), butyltrimethylammonium TFSI (BtMA-TFSI), methyltributylphosphonium TFSI (MtBPho-TFSI), Li-TFSI, Na-TFSI, Li bis(pentafluoroethanesulfonyl)imide (Li-PFSI), BMIM tetrafluoroborate (BMIM-BF₄), BMIM hexafluorophosphate (BMIM-PF₆), BMIM-FeCl₄, Na₂CO₃, and Li bis(oxalato)borate (Li-BOB) were purchased from TCI. The doping solvents *n*-butyl acetate (*n*BA) and dimethylformamide (DMF) were purchased from Wako. The molecular structures of these compounds are provided in Extended Data Fig. 1 in the main text.

1.2 Doping methodology

The PBTTT thin films were fabricated on standard EAGLE XG glass substrates, except for those intended for use in FTIR and PYS analyses. FTIR spectra were acquired on CaF_2 substrates purchased from the Pier Optics Co., Ltd., while PYS data were obtained on indium-tin-oxide (ITO) substrates. The PBTTT thin films were deposited via spin-coating from 1 wt% *o*DCB solutions with a spinning speed of 2000 rpm for 1 min. The resulting films were annealed on a hotplate at 180 °C for 1 h, then slowly cooled to room temperature. The film thicknesses were determined to be 42 ± 2 nm using a Dektak surface profilometer.

The PBTTT was doped simply by immersing solid-state thin films into dopant solutions for 10 min at 60 °C in N_2 -purged vials (commercially available, 7 mL). Doping solutions were prepared by dissolving F4TCNQ in the ionic liquids or by co-dissolving the F4TCNQ and the ionic solute in *n*BA. The combinations of solutes and solvents are listed in Supplementary Table 1. After cooling the vial to room temperature, the film was removed from the solution and residual solvent was evaporated under a flow of N_2 .

Initiator dopant	Ionic solute	solvent
F4TCNQ 0.6 wt%	-	EMIM-TFSI
F4TCNQ 0.6 wt%	-	BMIM-TFSI
F4TCNQ 0.6 wt%	-	BMIM-BF ₄
F4TCNQ 0.6 wt%	-	BMIM-PF ₆
F4TCNQ 0.6 wt%	-	BMIM-FAP
F4TCNQ 0.6 wt%	-	BMIM-FeCl ₄
F4TCNQ 0.6 wt%	Li-TFSI 3wt%	<i>n</i> BA
F4TCNQ 0.6 wt%	Na-TFSI 3wt%	<i>n</i> BA
F4TCNQ 0.6 wt%	Li-PFSI 3wt%	<i>n</i> BA
F4TCNQ 0.6 wt%	Li-BOB 3wt%	<i>n</i> BA
F4TCNQ 0.6 wt%	Na ₂ CO ₃ 3wt%	DMF
TCNQ 0.6 wt%	BMIM-TFSI 3wt%	<i>n</i> BA
TCNQ 0.6 wt%	Li-TFSI 3wt%	<i>n</i> BA

Supplementary Table 1: A summary of combinations of initiator dopant, ionic solute and solvent used in this work.

1.3 Doping characterization

UV-vis-NIR spectroscopy. Thin-film UV-vis-NIR spectra were acquired with specimens on glass substrates in air using a JASCO spectrometer (V-670).

FTIR spectroscopy. Thin-film FTIR spectra were collected on CaF_2 substrates in air using a JASCO spectrometer (FT/IR-4700).

ESR spectroscopy. X-band ESR data were acquired using a JEOL JES-X310 spectrometer. The sample was inserted into a quartz ESR tube and purged with helium gas for heat exchange. The ESR device was placed in a TE_{011} cylindrical cavity, in which the typical Q -factor was measured to be approximately 7000 – 8000 (sufficient for spin counting). In the case of low temperature measurements, a continuous He gas flow cryostat was used. The microwave power and modulation magnetic field were carefully adjusted to approximately 0.1 mW (depending on temperature) and 50 μT , respectively. The magnetic field and ESR intensity were calibrated with a standard $\text{Mn}^{2+}/\text{MgO}$ marker and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

ESR allows probing of the population of unpaired electron spins. The number of spins, N_{spin} , that contribute to the spin paramagnetic susceptibility can be evaluated by taking the double integral of the first derivative ESR spectra. It should be noted that, in the case of p-type conjugated polymers, positive charge carriers can form localized polarons ($+e$, $s = 1/2$), localized bipolarons ($+2e$, $s = 1/2$; sometimes referred to as polaron pairs) and delocalized hole states ($+e$, $s = 1/2$). Localized polarons are expected to contribute to the Curie susceptibility of the material, whereas delocalized holes contribute to the Pauli susceptibility. ESR is not able to detect spin singlet states (*i.e.* bipolarons or polaron pairs). ESR studies regarding gate-induced carrier spins have demonstrated that bipolarons become energetically favorable when the doping level exceeds 0.2 – 0.3 % with respect to the quantity of thiophene rings.^{26,27} Therefore, we can assume that positive carrier spins in PBTTT are likely to form either spin-singlet bipolarons (polaron pairs) or delocalized holes. In either case, the net spin susceptibility resulting from positive carriers in the PBTTT should be much less than the Curie susceptibility. In addition, closed-shell anions used as additional anions (*e.g.* BF_4^- and TFSI^-) do not contribute to spin paramagnetic susceptibility because the total angular momentum of closed-shell anions is zero. Therefore, it is reasonable to assume that the remaining F4TCNQ radical anions in the anion exchanged material contribute purely to spin-1/2 Curie susceptibility. Given the assumptions above,

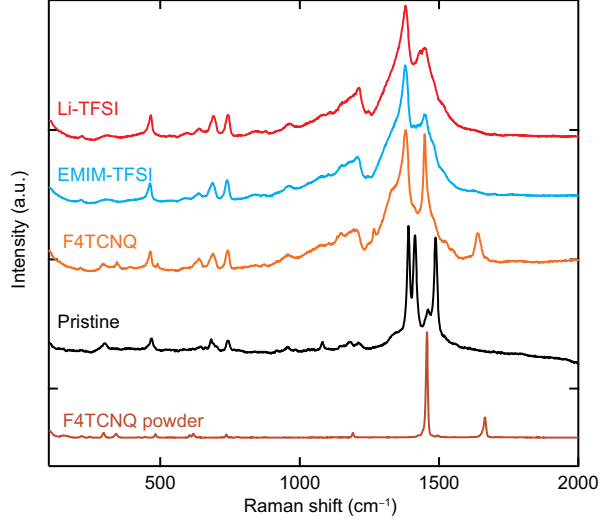
which have been verified in a previous study,^{28,29} we evaluated the residual amounts of F4TCNQ radical anions based on spin counting. We emphasize that these residual quantities were likely overestimated because a finite fraction of the localized polarons in the PBTTT may contribute to Curie susceptibility. Hence, the present spin counting provides the lower limit of the anion exchange efficiency (98 %), as discussed in the main text. To be able to exclude the contribution of intrinsic carrier concentration, the carrier concentration of undoped PBTTT was estimated by ESR. Because of highly resistive nature of undoped PBTTT (its resistance is on the order of TΩ), the Hall effect was not observed. In addition, there was no noticeable signal found in ESR measurements. Judging from the detection limit in an ESR equipment ($\sim 10^{11}$ spins), the intrinsic carrier concentration was estimated to be $4 \times 10^{17} \text{ cm}^{-3}$, which is negligibly small compared to doped state ($1.4 \times 10^{21} \text{ cm}^{-3}$) and is even smaller than residual F4TCNQ radical anion ($1.7 \times 10^{19} \text{ cm}^{-3}$) after anion exchange.

PYS measurements. PYS data were obtained using ITO substrates with a SUMIT-OMO PYS-202 instrument in vacuum.

Raman spectroscopy. Raman spectra were recorded on glass substrates with a HORIBA LabRAM HR-Evolution instrument and using a HeNe (633 nm) laser. Assignments of the Raman modes for neutral/anionic F4TCNQ and for neutral PBTTT are provided in Supplementary Tables 2 and 3. The absence of the F4TCNQ radical anion in the PBTTT was confirmed, *i.e.*, the peaks at 1449 and 1640 cm^{-1} , assigned to the C–CN, and C=C stretching modes of the F4TCNQ $\bullet^-$,³⁰ are generated only by the F4TCNQ-doped film (Fig. S1). The spectra for the anion exchange doped films are almost identical to that obtained from electrochemically-doped PBTTT.³¹

State	Raman shift (cm^{-1})	Description
Neutral	1457	C–CN stretching
Neutral	1665	C=C stretching
Neutral	2226	C $\equiv$ N stretching
Anion	1443	C–CN stretching
Anion	1641	C=C stretching
Anion	2205	C $\equiv$ N stretching

Supplementary Table 2: Raman mode assignment for neutral/anionic F4TCNQ.³⁰



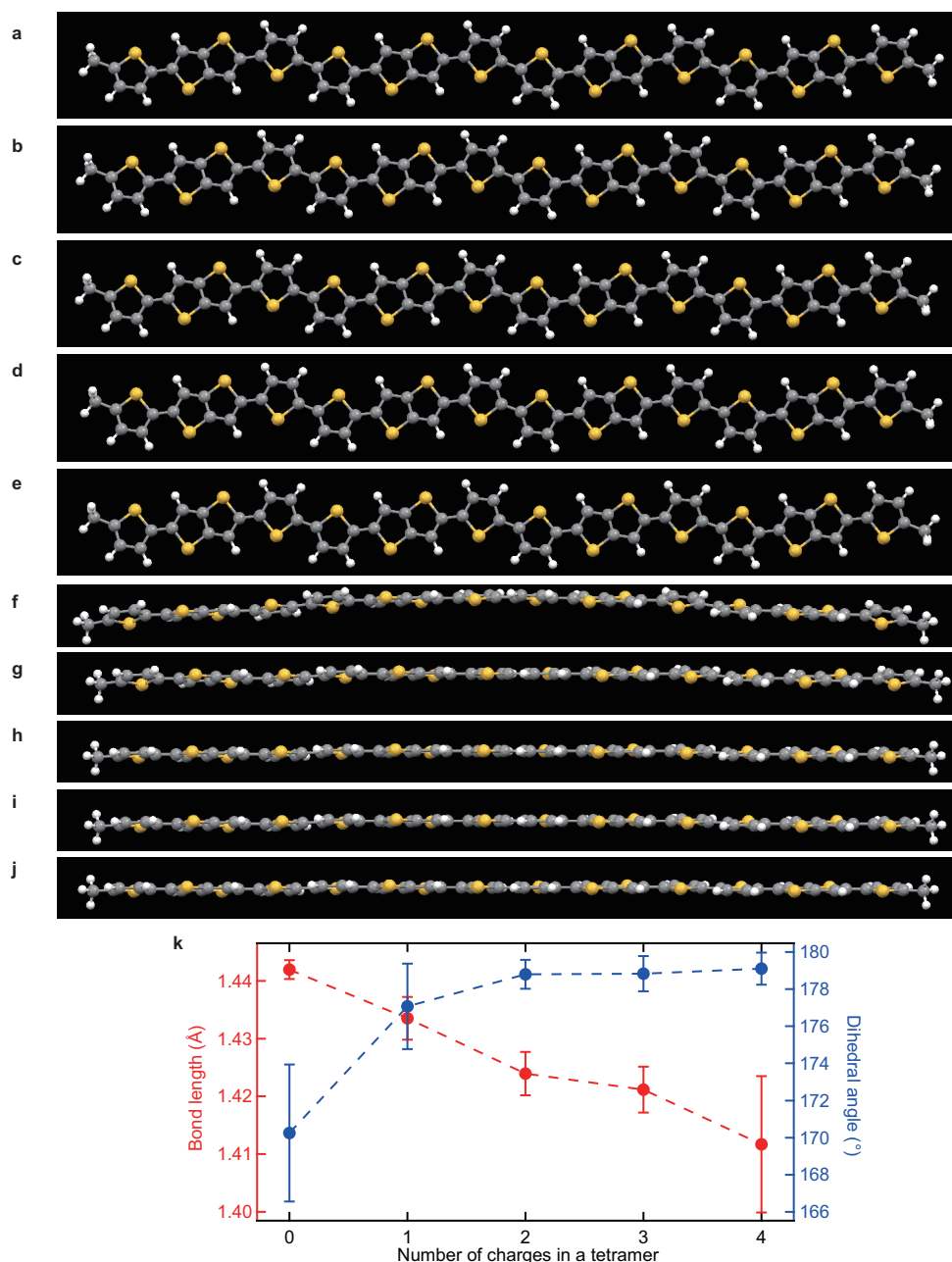
Supplementary Figure 1: Raman spectroscopy to assess residual anions in PBTTT thin films. Raman spectra of PBTTT-C14 thin films: pristine (black), F4TCNQ-doped (orange), anion exchange doped with EMIM-TFSI (light blue), and with Li-TFSI (red). The Raman spectrum of pristine F4TCNQ powder is also plotted (brown).

State	Raman shift (cm ⁻¹)	Description
Neutral	1393	C=C stretching
Neutral	1415	C=C stretching
Neutral	1488	C=C/C-C stretching/shrinking

Supplementary Table 3: Raman mode assignments for neutral PBTTT.³¹

XRD measurements. Out-of-plane XRD data were acquired using a RIGAKU Smart-Lab with a MicroMax-007HF X-ray generator, employing Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) in conjunction with a 0.1-mm-thick EAGLE XG glass substrate to reduce substrate scattering. In Fig. 4c in the main text, it is evident that the FWHM values decrease as the doping level increases, meaning that the extent of lattice disorder decreases dramatically. We note that the relaxation of torsion, tension and/or bending along the polymer backbones may result in crystal rearrangement. DFT calculations showed that the structure of highly-doped conducting polymer changes from benzenoid to quinoid, thus generating a planar conjugated backbone (Fig. S2).

According to XRD measurements, there is no apparent morphological change found before and after doping, *i.e.*, a terrace structure due to microcrystalline, lamellar nature of PBTTT preserves even after doping. In addition, because neither broadening nor splitting was observed in diffraction peaks, the incorporation of dopant can be homogeneous over an entire bulk of PBTTT thin film. Therefore, we analyzed magnetotransport data without assuming spatial distribution of dopants.



Supplementary Figure 2: Optimized structures of PBTTT tetramers in neutral and charged states. Molecular structures of PBTTT tetramers in neutral (a, f). and charged states with one (b, g), two (c, h), three (d, i), and four holes per tetramer (e, j). The structures were optimized by DFT calculations with the B3LYP functional and 6-31+G(d) basis set. **k.** Average thiophene-thiophene and thiophene-thienothiophene ring bond lengths and dihedral angles between rings. Each error bar shows one standard deviation. The shortened bond lengths between rings and planarized chains in the charged state are consistent with a transition to a quinoid structure from a benzenoid structure.

1.4 Characterization of ions based on DFT calculations

The strength of ionic interactions typically varies with the size of the ions. In this work, the ionic interactions of various cations and anions were modeled based on the effective radius of each ion, R_{eff} , defined as the radius of a sphere having a volume equal to the interior of the van der Waals surface of the ion, V_{ion} . This value was calculated as

$$R_{\text{eff}} = \left(\frac{3V_{\text{ion}}}{4\pi} \right)^{\frac{1}{3}}, \quad (1)$$

with the van der Waals surface defined as the surface based on a cut-off electron density isovalue of 0.002.³² These surfaces were determined by DFT calculations with the B3LYP functional and 6-311+G(d,p) basis set, using the Gaussian09 software package. In the case of Li^+ and Na^+ , the mean value of the standard ionic radius was employed. The calculated radius values are provided in Supplementary Table 4.

The ionic interactions of organic ions with unique shapes were also evaluated by mapping the electrostatic potentials using the Spartan'16 software package (Wavefunction, Inc.). Structures were optimized and electrostatic potentials were calculated with the B3LYP functional and 6-311+G(d,p) basis set. Smaller ions were found to have higher surface electrostatic potentials, and so the electrostatic potential mapping results generally agreed with the R_{eff} values.

Chemical hardness based on the hard and soft acid and base (HSAB) theory³² can also be used to characterize ions. This approach has been employed to predict various ionic phenomena, including ion exchange in which a hard ion is more likely to produce an ion pair with a hard counterion, and *vice versa*. In DFT, the chemical potential, μ , is defined as the derivative of the energy, E , with respect to the number of electrons, N , in a given environment with constant external potential, $v(r)$. The associated equation is

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v. \quad (2)$$

Chemical hardness, η , is then described as

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v = \frac{1}{2} (E_{N+1} - 2E_N + E_{N-1}). \quad (3)$$

In this work, the η value for each ion was calculated using DFT in conjunction with the B3LYP functional/6-311+G(d) basis set, and M06-2X functional/6-311+G(d) basis set, employing Gaussian09. These basis sets are known to perform better than others at a similar

Anions	R_{eff}
BF_4^-	2.43
PF_6^-	2.71
BOB^-	3.25
TFSI^-	3.50
PFSI^-	3.84
FAP^-	3.95

Cations	R_{eff}
Li^+	0.76
Na^+	1.19
EMIM^+	3.15
BtMA^+	3.38
BPyri^+	3.42
MPPyrr^+	3.42
BMIM^+	3.44
MtBPho^+	4.13

Supplementary Table 4: Calculated effective ion radius values for organic ions.

computational cost.³³ Prior to the calculation of energy values, the molecular structure of each ion was optimized with the B3LYP functional and 6-311+G(d) basis set for the singly charged ground state. The results of these calculations are summarized in Supplementary Table 5.

The resulting η values based on HSAB theory explain the majority of our experimental results obtained from anion exchange doping. That is, the optimal doping efficiency is achieved when the softest Y^- and the hardest X^+ are used, with $\text{X}^+ = \text{MtBPho}^+$ being the exception. This discrepancy likely occurred because the relatively long alkyl chains in MtBPho^+ are not taken into account when assessing chemical hardness, even though they have a significant effect on the van der Waals surface of the ion. Although chemical hardness does not predict the entire trend of efficiency values obtained from anion exchange doping, particularly in the case of bulky organic ions, standard HSAB theory is evidently generally

Anions	η by B3LYP (eV)	η by M06-2X (eV)
PF_6^-	6.65	7.36
BF_4^-	6.39	6.94
FAP^-	5.41	5.85
TFSI^-	5.38	5.78
PFSI^-	5.24	5.66
BOB^-	4.87	5.37

Cations	η by B3LYP (eV)	η by M06-2X (eV)
Li^+	35.2	35.3
Na^+	21.1	21.1
BtMA^+	6.17	6.43
MtBPho^+	5.56	6.02
EMIM^+	5.45	5.60
BPyri^+	4.94	5.13
MPPyrr^+	4.83	4.98

Supplementary Table 5: Chemical hardness values for organic ions. Values for anions are taken from the literature.³³ Values for cations were calculated using the same method as applied for the anions.

applicable to the analysis of anion exchange phenomena in solid state thin films. In addition to electrostatic potential mapping, more detailed chemical hardness calculations that include effects such as conformation, solvation and polarization of each ion pair, should allow a more in-depth understanding of anion exchange doping in future.

1.5 Estimation of energy gain by anion exchange

This work demonstrated that the doping level in PBTTT thin films is improved dramatically as a result of anion exchange doping, due to the reaction



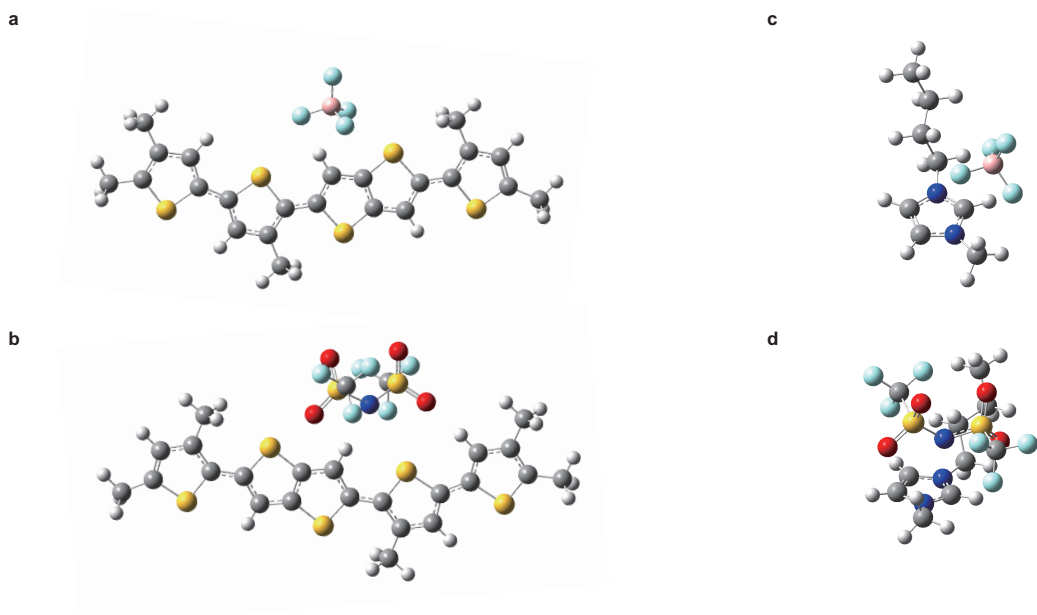
Spectroscopic analyses show that the anion exchange reaction in Eq. (4) proceeds spontaneously. We estimated the energy gain associated with anion exchange by defining the energy gain, ΔE_{ex} , for the creation of ion pairs without solvation and intercalation between multiple ions as

$$\Delta E_{\text{ex}} = [E(\text{PBTTT}^{\bullet+}\text{Y}^-) + E(\text{X}^+\text{F4TCNQ}^{\bullet-})] - [E(\text{PBTTT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{X}^+\text{Y}^-)], \quad (5)$$

where $E(\text{X}^+\text{Y}^-)$ is the total energy of the $[\text{X}^+\text{Y}^-]$ ion pair. The conformational search to obtain the total energy of ion pairs was carried out using DFT calculations with the M06-2X functional and 6-31++G(d,p) basis set. Because the dopant molecules are situated within the alkyl side chain regions in the PBTTT thin films, as shown by the XRD data presented in the main text, the initial $\text{PBTTT}^{\bullet+}$ and Y^- ion pair was set such that Y^- approached the alkyl side chains. To reduce calculation costs, the alkyl chains were replaced with methyl groups and the $\text{PBTTT}^{\bullet+}$ monomer was employed. During the optimization, the structure of $\text{PBTTT}^{\bullet+}$ was fixed in order to reduce the calculation costs, which may also help to avoid unrealistic torsion of the ion and better reproduce the actual conformation.

Comparison between TFSI⁻ and BF₄⁻

Optimized structures for [PBTtT^{•+}BF₄⁻] and [PBTtT^{•+}TFSI⁻] are shown in Figs. S3a and b. The optimum conformations for [BMIM⁺BF₄⁻] and [BMIM⁺TFSI⁻] were determined from the literature (Figs. S3c and d).³⁴ Note that, for the [PBTtT^{•+}F4TCNQ^{•-}] ion pair, F4TCNQ^{•-} is not necessarily situated on a single PBTtT backbone but rather on multiple backbones. In addition, an ion pair composed of F4TCNQ^{•-} in solution has various possible conformations, and optimization of such conformations requires a special care. To avoid failure of the calculations, we did not proceed with the total energy calculation for this intermediate ion pair but rather compared the total energies for the final states of anion exchanged PBTtT models, *i.e.*, we compared the change in energies for anion exchange with BF₄⁻ and TFSI⁻ in the following procedures without calculating ion pairs with F4TCNQ^{•-}.



Supplementary Figure 3: Optimized structures of ion pairs. a. [PBTtT^{•+}BF₄⁻], b. [PBTtT^{•+}TFSI⁻], c. [BMIM⁺BF₄⁻] and d. [BMIM⁺TFSI⁻].

The total energy values for the ion pairs were determined using the M06-2X functional because this is known to perform better than the B3LYP functional.³⁴ It is evident from Eq. (4) that the energy gains for two different anions TFSI⁻ and BF₄⁻ are given by

$$\Delta E_{\text{ex}}^{\text{TFSI}} = [E(\text{PBTtT}^{\bullet+}\text{TFSI}^-) + E(\text{BMIM}^+\text{F4TCNQ}^{\bullet-})] - [E(\text{PBTtT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{BMIM}^+\text{TFSI}^-)] \quad (6)$$

and

$$\Delta E_{\text{ex}}^{\text{BF}_4^-} = [E(\text{PBTtT}^{\bullet+} \text{BF}_4^-) + E(\text{BMIM}^+ \text{F4TCNQ}^{\bullet-})] - [E(\text{PBTtT}^{\bullet+} \text{F4TCNQ}^{\bullet-}) + E(\text{BMIM}^+ \text{BF}_4^-)]. \quad (7)$$

Because the second and third terms in Eqs. (6) and (7) are identical, the difference in energy gain between anion exchange doping with TFSI[−] and with BF₄[−] can be determined by subtracting Eq. (7) from Eq. (6) to give

$$\Delta E_{\text{ex}}^{\text{TFSI}^-} - \Delta E_{\text{ex}}^{\text{BF}_4^-} = [E(\text{PBTtT}^{\bullet+} \text{TFSI}^-) - E(\text{BMIM}^+ \text{TFSI}^-)] - [E(\text{PBTtT}^{\bullet+} \text{BF}_4^-) - E(\text{BMIM}^+ \text{BF}_4^-)]. \quad (8)$$

The total energies obtained from DFT calculations are summarized in Table 6, and the difference in energy gain between anion exchange with TFSI[−] and BF₄[−] is calculated to be approximately −150 meV (−0.0055 hartree), *i.e.*, $\Delta E_{\text{ex}}^{\text{TFSI}^-} - \Delta E_{\text{ex}}^{\text{BF}_4^-} = -150$ meV. This simplistic model explains why anion exchange reduces the total energy in the hybrid anion system, and why ion exchange efficiency scales with ionic interaction strength. In addition, the predicted preference for anion exchange with TFSI[−] compared to BF₄[−] agrees with the experimental results presented in the main text.

Ion pair	Total energy (hartree)	
PBTtT ^{•+} BF ₄ [−]	−3303.2261	Fig. S3a
PBTtT ^{•+} TFSI [−]	−4705.6659	Fig. S3b
BMIM ⁺ BF ₄ [−]	−847.5624	Fig. S3c
BMIM ⁺ TFSI [−]	−2249.9967	Fig. S3d

Supplementary Table 6: Calculated total energy values for ion pairs. The total energy values for ion pairs as calculated using the M06-2X functional and the 6-31++G(d,p) basis set.

Conformation effect

In the previous section, we have intentionally avoided the calculation associated with ion pairs of F4TCNQ $\bullet^-$ (*i.e.*, [X $^+$ F4TCNQ $\bullet^-$]) because its conformation in solution is reported to be complicated.^{35,36} Although there remains considerable debate on the conformation effect in anion exchange phenomena, we also calculated the absolute value of $\Delta E_{\text{ex}}^{\text{TFSI}}$ based on equation (5) for anion exchange with EMIM-TFSI and with Li-TFSI. It is found that the experimentally-verified binding preference can be explained by taking into account dimerization of F4TCNQ radical anions through $\pi - \pi$ interactions.^{37,38}

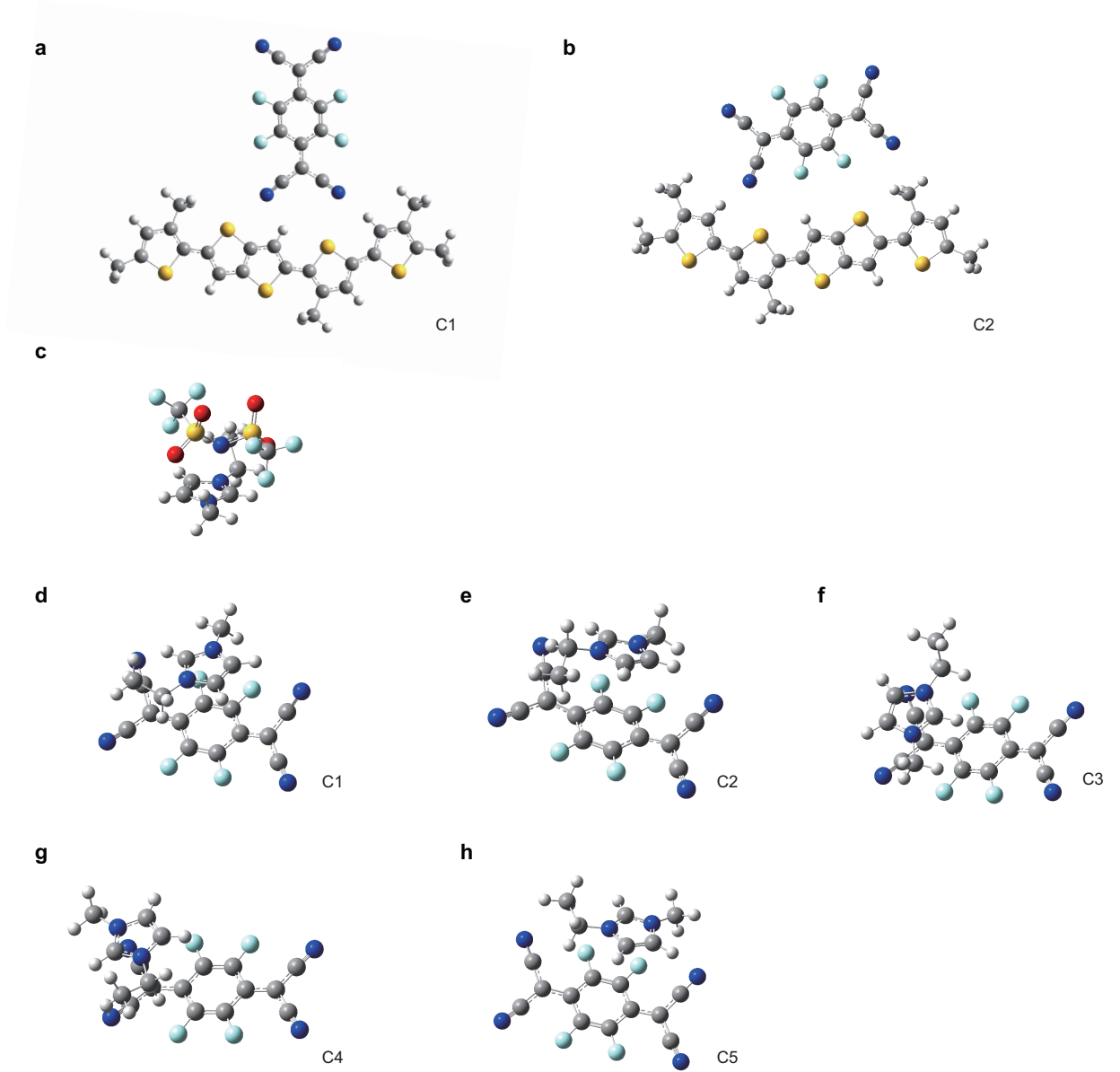
EMIM $^+$ is chosen as an example of organic cation X $^+$ because it possesses shorter alkyl chains compared to other imidazolium based cations, which saves efforts for searching optimized structures. To calculate $\Delta E_{\text{ex}}^{\text{TFSI}}$ for anion exchange with EMIM-TFSI, the optimized structure shown in Fig. S3b was employed for [PBTTT $\bullet^+$ TFSI $^-$], and a reported structure³⁴ was employed for [EMIM $^+$ TFSI $^-$]. Optimization of structures of [PBTTT $\bullet^+$ F4TCNQ $\bullet^-$] was conducted in a similar manner to that of [PBTTT $\bullet^+$ TFSI $^-$] or [PBTTT $\bullet^+$ BF $_4^-$].

In the conformation 1 (C1), negatively charged cyano group in F4TCNQ $\bullet^-$ points to PBTTT $\bullet^+$ (Fig. S4a). In C2, the long axis of F4TCNQ $\bullet^-$ and PBTTT $\bullet^+$ are parallel each other (Fig. S4b). C2 is slightly unfavorable in energy as shown in Supplementary Table 7, and might be unrealistic because of steric hindrance of alkyl chains of PBTTT. Thus, we employed C1 in the following calculations. Optimization of structures for [EMIM $^+$ F4TCNQ $\bullet^-$] includes the search for various conformations in solution. Figures S4d-g show possible conformations that we found (C1 – C5), whose total energies are shown in Supplementary Table 7.

The optimizations of structures in anion exchange with Li-TFSI were also conducted. In this calculation, two conformations for [Li $^+$ TFSI $^-$] (Figs. S5a, b) and five conformations for [Li $^+$ F4TCNQ $\bullet^-$] were considered (Figs. S5c-g), while the conformation of other ion pairs were identical to those in anion exchange with EMIM-TFSI. Calculated total energies of ion pairs are shown in Supplementary Table 8.

The energy gain for EMIM-TFSI anion exchange is given by

$$\begin{aligned} \Delta E_{\text{ex}}^{\text{EMIM-TFSI}} = & [E(\text{PBTTT}\bullet^+\text{TFSI}^-) + E(\text{EMIM}^+\text{F4TCNQ}\bullet^-)] \\ & - [E(\text{PBTTT}\bullet^+\text{F4TCNQ}\bullet^-) + E(\text{EMIM}^+\text{TFSI}^-)] \end{aligned} \quad (9)$$



Supplementary Figure 4: Optimized structures of ion pairs in anion exchange with EMIM-TFSI. a, b. C1 and C2 of $[\text{PBTtT}^{\bullet+}\text{F4TCNQ}^{\bullet-}]$. **c.** $[\text{EMIM}^+\text{TFSI}^-]$, **d - h.** C1-C5 of $[\text{EMIM}^+\text{F4TCNQ}^{\bullet-}]$.

and that for Li-TFSI anion exchange is

$$\begin{aligned} \Delta E_{\text{ex}}^{\text{Li-TFSI}} = & [E(\text{PBTtT}^{\bullet+}\text{TFSI}^-) + E(\text{Li}^+\text{F4TCNQ}^{\bullet-})] \\ & - [E(\text{PBTtT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{Li}^+\text{TFSI}^-)] \end{aligned} \quad (10)$$

Using the most stable conformations, $\Delta E_{\text{ex}}^{\text{EMIM-TFSI}}$ is calculated to be 117 meV (0.0043 hartree) and $\Delta E_{\text{ex}}^{\text{Li-TFSI}}$ is calculated to be 928 meV (0.0341 hartree), respectively. The

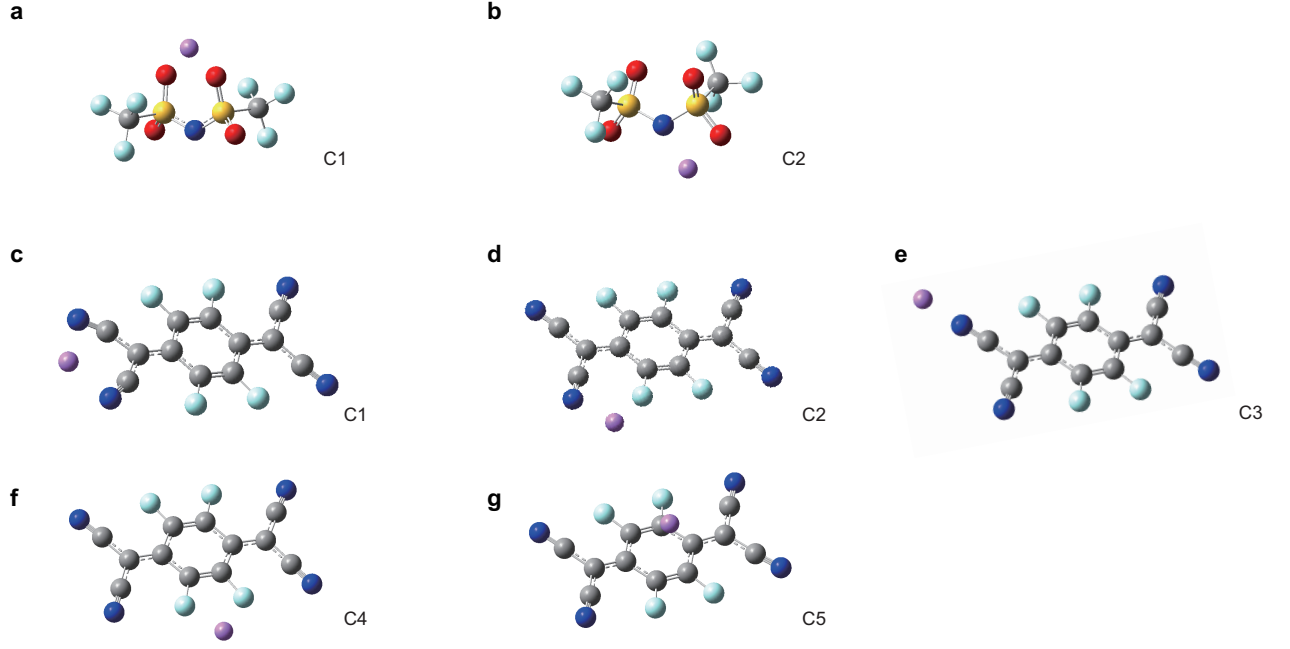
Ion pair	Total energy (hartree)	
C1 PBTTT ^{•+} F4TCNQ ^{•-}	-3954.0639	Fig. S4a
C2 PBTTT ^{•+} F4TCNQ ^{•-}	-3954.0622	Fig. S4b
EMIM ⁺ TFSI ⁻	-2171.4040	Fig. S4c
C1 EMIM ⁺ F4TCNQ ^{•-}	-1419.7977	Fig. S4d
C2 EMIM ⁺ F4TCNQ ^{•-}	-1419.7976	Fig. S4e
C3 EMIM ⁺ F4TCNQ ^{•-}	-1419.7944	Fig. S4f
C4 EMIM ⁺ F4TCNQ ^{•-}	-1419.7942	Fig. S4g
C5 EMIM ⁺ F4TCNQ ^{•-}	-1419.7935	Fig. S4h

Supplementary Table 7: Calculated total energy values for ion pairs in anion exchange with EMIM-TFSI. The total energy values for ion pairs as calculated using the M06-2X functional and the 6-31++G(d,p) basis set.

Ion pair	Total energy (hartree)	
C1 Li ⁺ TFSI ⁻	-1834.3701	Fig. S5 a
C2 Li ⁺ TFSI ⁻	-1834.3536	Fig. S5 b
C1 Li ⁺ F4TCNQ ^{•-}	-1082.7341	Fig. S5c
C2 Li ⁺ F4TCNQ ^{•-}	-1082.7328	Fig. S5d
C3 Li ⁺ F4TCNQ ^{•-}	-1082.7284	Fig. S5e
C4 Li ⁺ F4TCNQ ^{•-}	-1082.7067	Fig. S5f
C5 Li ⁺ F4TCNQ ^{•-}	-1082.6927	Fig. S5g

Supplementary Table 8: Calculated total energy values for ion pairs for anion exchange with Li-TFSI. The total energy values for ion pairs as calculated using the M06-2X functional and the 6-31++G(d,p) basis set.

positive value in the energy gain means that the anion exchange is energetically unfavorable, which clearly contradicts to the experimental result. We infer from previous literature that the calculation failure stems largely from the conformation search for ion pairs with F4TCNQ^{•-}. One possible factor is dimerization of TCNQ in solution via π - π interaction to form TCNQ₂^{•-} or TCNQ₂²⁻, which has been reported experimentally and theoretically.^{37,38} Although we do not have evidence of existence of F4TCNQ dimers in the present sys-



Supplementary Figure 5: Optimized structures of ion pairs in anion exchange with Li-TFSI. a, b. C1 and C2 of $[\text{Li}^+\text{TFSI}^-]$. **c-g.** C1 – C5 of $[\text{Li}^+\text{TFSI}^-]$. Li^+ is situated in the same plane of $\text{F4TCNQ}_2^{\bullet-}$ for **c - f**.

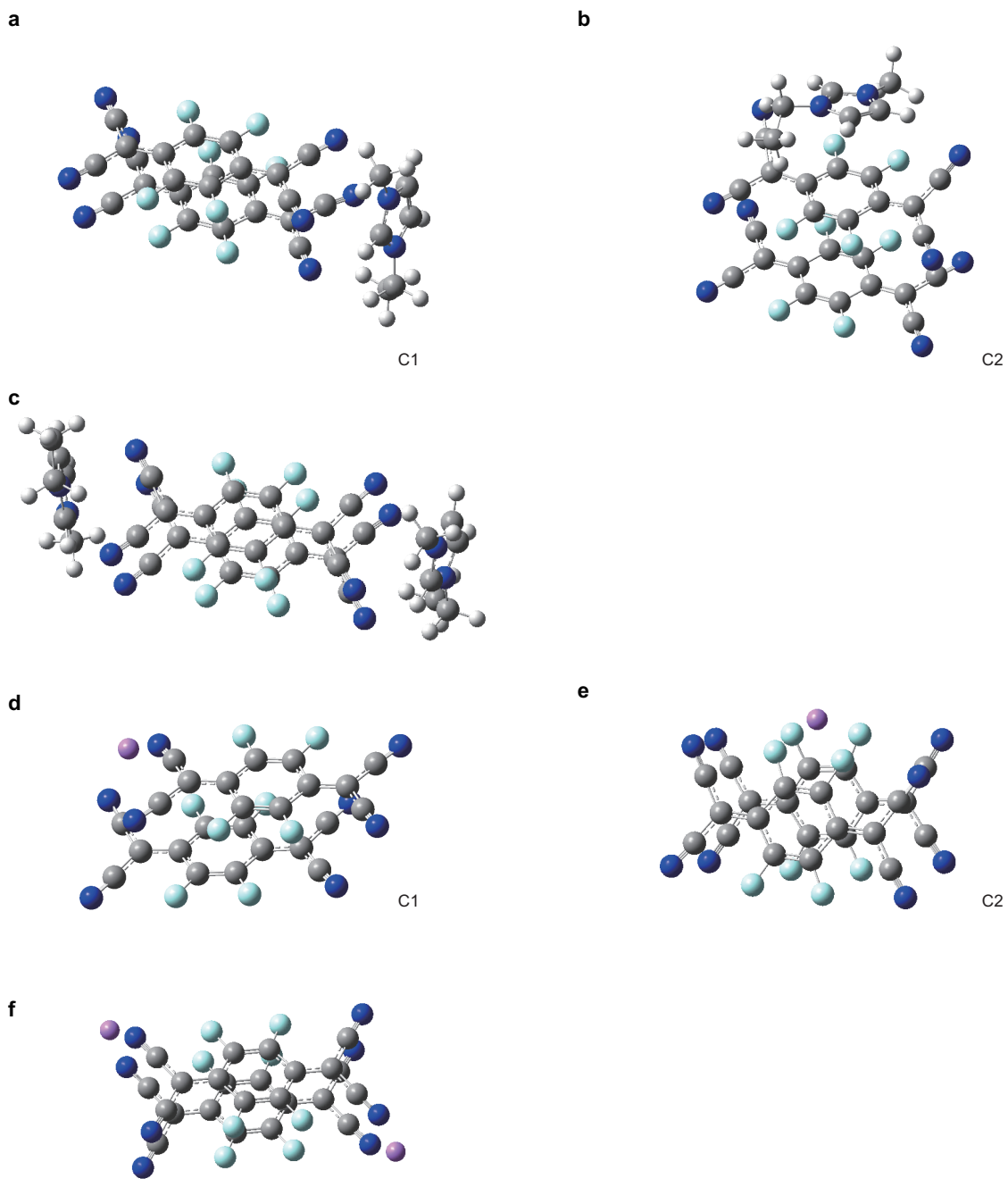
tem, the calculation taking into account the dimerization effect was also conducted. Possible conformations of $[\text{EMIM}^+\text{F4TCNQ}_2^{\bullet-}]$, $[\text{EMIM}_2^{2+}\text{F4TCNQ}_2^{2-}]$, $[\text{Li}^+\text{F4TCNQ}_2^{\bullet-}]$ and $[\text{Li}_2^{2+}\text{F4TCNQ}_2^{2-}]$ were further optimized (Fig. S6 and Table 9). The most energetically-favorable conformation is found when F4TCNQ molecules interact with cations with their negatively charged cyano groups, which has been reported in a literature.³⁸

The energy gain is similarly calculated as;

$$\Delta E_{\text{ex}'}^{\text{EMIM-TFSI}} = [E(\text{PBTtT}^{\bullet+}\text{TFSI}^-) + E(\text{EMIM}^+\text{F4TCNQ}_2^{\bullet-})] - [E(\text{PBTtT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{EMIM}^+\text{TFSI}^-) + E(\text{F4TCNQ})] \quad (11)$$

$$\Delta E_{\text{ex}'}^{\text{EMIM-TFSI}} = [E(\text{PBTtT}^{\bullet+}\text{TFSI}^-) + \frac{1}{2}E(\text{EMIM}_2^{2+}\text{F4TCNQ}_2^{2-})] - [E(\text{PBTtT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{EMIM}^+\text{TFSI}^-)] \quad (12)$$

$$\Delta E_{\text{ex}'}^{\text{Li-TFSI}} = [E(\text{PBTtT}^{\bullet+}\text{TFSI}^-) + E(\text{Li}^+\text{F4TCNQ}_2^{\bullet-})] - [E(\text{PBTtT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{Li}^+\text{TFSI}^-) + E(\text{F4TCNQ})] \quad (13)$$



Supplementary Figure 6: Optimized structures of ion pairs with F4TCNQ dimer. a. [EMIM⁺F4TCNQ₂^{•-}], **b.** [Li⁺F4TCNQ₂^{•-}].

$$\Delta E_{\text{ex}''}^{\text{Li-TFSI}} = [E(\text{PBTTT}^{\bullet+}\text{TFSI}^-) + \frac{1}{2}E(\text{Li}_2^2+\text{F4TCNQ}_2^{2-})] - [E(\text{PBTTT}^{\bullet+}\text{F4TCNQ}^{\bullet-}) + E(\text{Li}^+\text{TFSI}^-)] \quad (14)$$

For anion exchange with EMIM-TFSI, values with F4TCNQ₂^{•-} and F4TCNQ₂²⁻ were cal-

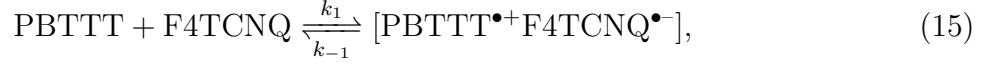
Ion pair	Total energy (hartree)	
C1 EMIM ⁺ F4TCNQ ₂ ^{•-}	-2494.9544	Fig. S6a
C2 EMIM ⁺ F4TCNQ ₂ ^{•-}	-2494.9454	Fig. S6b
EMIM ₂ ²⁺ F4TCNQ ₂ ²⁻	-2839.6374	Fig. S6c
C1 Li ⁺ F4TCNQ ₂ ^{•-}	-2157.9120	Fig. S6d
C2 Li ⁺ F4TCNQ ₂ ^{•-}	-2157.8613	Fig. S6e
Li ₂ ²⁺ F4TCNQ ₂ ²⁻	-2165.5617	Fig. S6f
F4TCNQ	-1075.1268	

Supplementary Table 9: Calculated total energy values to consider F4TCNQ dimerization. The total energy values for ion pairs and a molecule as calculated using the M06-2X functional and the 6-31++G(d,p) basis set.

culated to be $\Delta E_{\text{ex}'}^{\text{EMIM-TFSI}} = -696$ meV (-0.0256 hartree) and $\Delta E_{\text{ex}''}^{\text{EMIM-TFSI}} = -455$ meV (-0.0167 hartree). For anion exchange with Li-TFSI, these values were $\Delta E_{\text{ex}'}^{\text{Li-TFSI}} = -463$ meV (-0.0170 hartree) and $\Delta E_{\text{ex}''}^{\text{Li-TFSI}} = -345$ meV (-0.0127 hartree). In both cases, it is found that anion exchange can reduce the total energy in the hybrid anion system. From the present calculations, we found that conformation effects specifically of ion pairs with F4TCNQ^{•-} in solution should play the vital role to promote anion exchange in the present hybrid anion system. We should emphasize again that the most confident estimation of the total energy is given only when the complex conformational search is not required. This is the reason why we proceeded the calculation of difference in energy gain between TFSI⁻ and BF₄⁻ based on Eq. (8). Clearly, future work is needed to clarify the mechanism of anion exchange doping phenomena, and we hope that our work will encourage theoretical and electrochemical works to develop an accurate model in which kinetic and thermodynamic evidences for anion exchange in a solid state can be interpreted quantitatively.

1.6 Kinetics of anion exchange doping

As discussed in the main text, anion exchange drastically improves the doping concentration compared to conventional molecular doping. Here, we discuss the kinetics of anion exchange doping using a simple equilibrium model. In conventional molecular doping, charge transfer and back transfer between PBTTT and the dopant (F4TCNQ) should be in equilibrium at a given doping concentration, such that



where k_1 and k_{-1} are the reaction rate constants for charge transfer and charge back-transfer at a given doping level. The equilibrium constant, K_1 , can be written as

$$K_1 = \frac{[\text{PBTTT}^{\bullet+}\text{F4TCNQ}^{\bullet-}]}{[\text{PBTTT}][\text{F4TCNQ}]}. \quad (16)$$

In the anion exchange doping process, anion exchange occurs after the initial charge transfer process between PBTTT and F4TCNQ, and so



where k_2 and k_{-2} are the reaction rate constants for the anion exchange ($\text{F4TCNQ}^{\bullet-} \rightarrow \text{Y}^-$) and for the reverse reaction, respectively. The equilibrium constant, K_2 , is therefore

$$K_2 = \frac{[\text{PBTTT}^{\bullet+}\text{Y}^-][\text{X}^+][\text{F4TCNQ}^{\bullet-}]}{[\text{PBTTT}^{\bullet+}\text{F4TCNQ}^{\bullet-}][\text{X}^+][\text{Y}^-]}. \quad (18)$$

If the product after anion exchange doping is thermodynamically stable and activity of Y^- is higher than that of $\text{F4TCNQ}^{\bullet-}$, this equilibrium is biased to the right. The anion exchange reaction therefore occurs with an exchange efficiency of nearly unity when an optimized combination of X^+ and Y^- exists in solution with reasonably-high concentration, as confirmed by the various spectroscopic analyses. This efficient anion exchange reaction decreases the population of $[\text{PBTTT}^{\bullet+}\text{F4TCNQ}^{\bullet-}]$, which promotes the forward reaction in Eq. (15). Thus, the anion exchange reaction enhances the initial charge transfer between the PBTTT and F4TCNQ based on this equilibrium bias, and higher doping concentrations can be achieved compared to those obtained from conventional molecular doping.

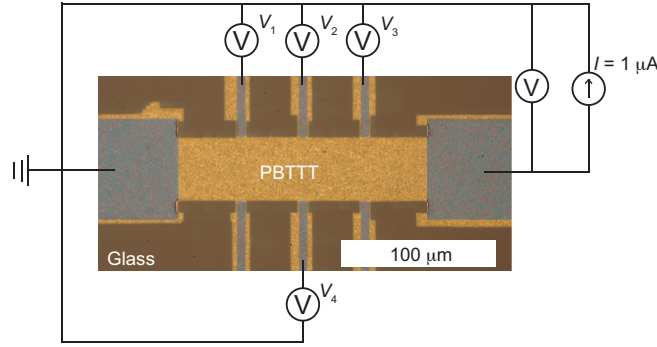
In the main text, we developed the anion exchange scenario with a two-step process; (i) doping initiation by F4TCNQ (Eq. (15)), then (ii) anion exchange by the second anion

Y^- (Eq. (17)). The two-step process in anion exchange doping could be intuitive because the step (i) is realized commonly in a conventional binary system (*e.g.*, PBTTT/F4TCNQ). Although the two-step scenario allows a qualitative analysis of energies and rate reaction, evidence of two-step process was yet to be presented so far, in particular an intermediate is hardly identified in this work. Instead of the proposed two-step process, one may think that the whole process occurs in a single step; *i.e.*, Y^- makes an ion-pair with PBTTT without formation of any intermediate, while F4TCNQ works as an oxidant. However, we presume that the proposed two-step process can be kinetically favorable compared to the single-step process as following reasons. From Marcus theory, charge transfer reactions between molecules take place through overlaps of donor and acceptor orbitals. Typically, this electronic coupling decays exponentially with the separation between donor and acceptor orbitals; $\exp(-\beta_s(r - r_0))$, with β_s as the decay constant, r as the separation of molecules, and r_0 as a sum of van der Waals radii of the both molecules.³⁹ Following this relationship with a commonly observed β_s of $1 \text{ \AA}^{-1}$,⁴⁰ the intermediate ion-pair should be present within an angstrom length scale. Thus, F4TCNQ and PBTTT are in close contact during the charge transfer process, and the intermediate $[\text{PBTTT}^{\bullet+}\text{F4TCNQ}^{\bullet-}]$ is expected to form for a finite period of time. It is more reasonable to consider that anion exchange with the second Y^- follows soon after formation of the intermediate ion-pair.

While the two-step model seems to be reasonable, we envisage an alternative scenario to explain efficient chemical doping in the present multi-ion system. A key to boost doping efficiency is redox potential of dopant, F4TCNQ. The redox potential of the dopant half-cell reaction, *e.g.*, $\text{F4TCNQ} + e^- \rightarrow \text{F4TCNQ}^{\bullet-}$, can become energetically favorable in the presence of spectator cations. This trend becomes more positive when the spectator cation becomes smaller ($\text{MtBPho}^+ \rightarrow \text{EMIM}^+ \rightarrow \text{Li}^+$) because of Coulombic association with the $\text{F4TCNQ}^{\bullet-}$ product. Because anions (TFSI^- , FAP^- , etc) have an impact on association with cations, the redox potential of F4TCNQ decreases when anions become harder *i.e.*, $\text{TFSI}^- \rightarrow \text{FAP}^- \rightarrow \text{PF6}^- \rightarrow \text{BF4}^-$. This alternative scenario does not contradict our experimental results. In either scenario, an intermediate of ion-pair is present at the very early stage of one-electron charge transfer process as following Marcus theory. Thus, we presume that that regardless of intermediate species, anion exchange takes place to produce the final product $[\text{PBTTT}^{\bullet+}Y^-]$. Again, high doping concentrations can be achieved when the anion exchange reaction decreases the population of intermediate.

1.7 Device fabrication and magnetotransport measurements

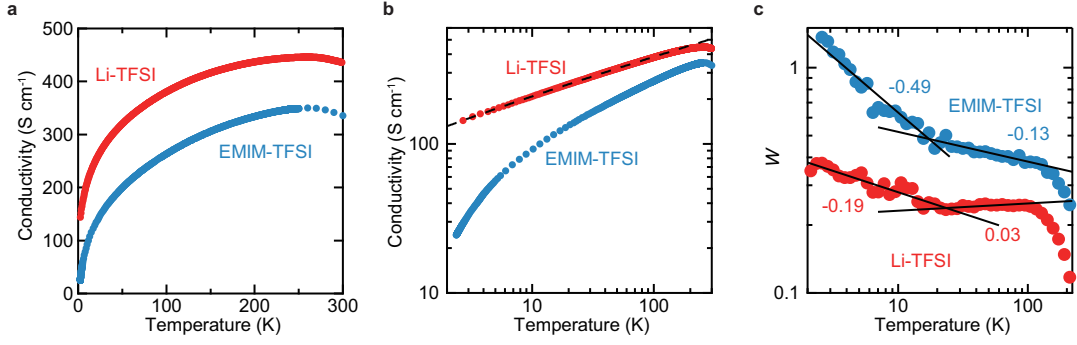
Device fabrication. Hall effect and magnetoconductance measurements were performed using a Hall bar geometry, with the doped PBTTT thin film patterned to allow precise measurement of the local potentials of probes along a channel. The Hall bar devices were fabricated on a 0.7-mm-thick EAGLE XG glass substrate that was pre-cleaned by sonication in acetone and isopropanol. Cr (3 nm) and Au (40 nm) electrodes were thermally evaporated through a shadow mask to form a channel length (L) and channel width (W) of $160\ \mu\text{m}$ and $40\ \mu\text{m}$, respectively. After evaporation of the electrodes, the devices were further cleaned with acetone and isopropanol. The PBTTT thin film was formed in a similar manner to that employed in preparation for spectroscopic characterization, and then patterned into the Hall bar geometry by laser etching using an yttrium aluminum garnet (YAG) laser. After the doping process, each device was encapsulated with CYTOP 809M (AGC Chemicals). A photographic image of the Hall bar used in this work is shown in Fig. S7.



Supplementary Figure 7: A photographic image of the Hall bar used in this work.

An optical microscopy image of the Hall bar used for magnetotransport measurements. A PBTTT thin film was patterned into the Hall bar geometry by laser etching, applying a channel length, L , and channel width, W , of 160 and $40\ \mu\text{m}$, respectively. Four-point-probe conductivity values and Hall coefficients were determined using longitudinal voltage probes V_1 , V_2 and V_3 and transverse probes $V_2 - V_4$.

Magnetotransport measurements. Magnetotransport measurements were performed using a He gas exchanged cryostat with a superconducting magnet (Mercury System, Oxford Instruments) along with a KEITHLEY 2400 source meter and KEYSIGHT 34465A 6 1/2 digital multimeter. Both the longitudinal and transverse electromotive forces were monitored



Supplementary Figure 8: Temperature dependence of the conductivity of anion exchange doped PBTTT thin films. The effects of temperature on the four terminal conductivity of EMIM-TFSI and Li-TFSI anion exchange doped PBTTT thin films in the form of (a.) linear and (b.) log-log plots. (c.) The temperature dependence analyzed using a Zabrodski plot.

simultaneously while applying a dc current of $1 \mu\text{A}$ and sweeping the magnetic field from 10 T to -10 T at a rate of 0.4 T min^{-1} .

The temperature dependence of the four-terminal conductivity was ascertained using the same Hall bar geometry employed for the magnetotransport measurements shown in Supplementary Figs. S8a and b. The effects of temperature on the conductivity of anion exchanged PBTTT thin films with Li-TFSI (red) and with EMIM-TFSI (blue) were analyzed based on the variable range hopping (VRH) model, $\sigma = \sigma_0 \exp \frac{T_0}{T} \frac{-1}{d}$, where T_0 is a characteristic temperature.⁴¹ In the general Mott VRH, d represents the dimensionality of charge transport, such that $d = 4$ for three dimensional VRH and $d = 3$ for two dimensional VRH. When taking into account the Coulomb interactions between localized sites, a soft gap appears in the density-of-states near the Fermi energy. Modification of the pure Mott VRH model yields the Efros-Shklovskii VRH (ES-VRH) model, which predicts $d = 2$. Because the exponent d plays a decisive role in understanding the charge transport mechanism, we employed so-called Zabrodskii plots, where $W = d \ln \sigma / d \ln T$ is plotted with respect to temperature (T) (Fig. S8c), such that the slope equals $-1/d$. The EMIM-TFSI anion exchanged PBTTT thin film shows $d = 2$, in agreement with the ES-VRH model, whereas the value of d for the Li-TFSI anion exchanged film does not match any possible VRH value, and instead shows a power law dependence, as is also confirmed by Fig. 8b. The weak effect of temperature on conductivity observed for the highly-doped PBTTT thin films indicates that these systems approach a metal-insulator transition.⁴²

Prior to magnetotransport measurements, we confirmed that all six potential probes in the channel measured the ideal local potential expected from the Hall bar geometry. As a result, the voltage drop due to the contact resistance at the channel/electrode contacts was estimated to be less than 0.1 % of the effective voltage applied along the channel. Each Hall voltage was measured as the transverse voltage, $V_{\text{trans}}(B) = V_2(B) - V_4(B)$. The Hall coefficient, R_H , and Hall mobility, μ_H , were extracted in the standard manner, via the equations

$$R_H = \frac{V_{\text{trans}}d}{IB} \quad (19)$$

and

$$\mu_H = |R_H|\sigma, \quad (20)$$

where d is the thickness of the doped PBTTT layer and σ is the four-point-probe conductivity. The latter value is determined from $\sigma = \frac{I}{V_{\text{long}}} \frac{L^*}{Wd}$, where V_{long} is the longitudinal voltage measured as $V_{\text{trans}}(B) = V_3 - V_1$ and L^* is the distance between probes V_3 and V_1 . It should be noted that the measured transverse voltage often contains a B -independent offset voltage and, during the analysis, a constant offset voltage V_{trans} was subtracted. In addition, a B -dependent offset voltage due to the contribution of longitudinal magnetoconductance is often observed in conducting polymers.⁴³ As an example, a quadratic voltage appears in addition to V_{trans} in Fig. 4e in the main text. Because the origin of the B -dependent offset voltage is trivial (*i.e.*, it results from the contribution of magnetoconductance due to weak localization)^{28,29} and it is an even function of B , the actual Hall voltage (which is a linear function of B) can be extracted by finding the difference in V_{trans} values under positive and negative magnetic fields. The Hall carrier concentration, n_{Hall} , can be extracted from the results of these calculations as $n_{\text{Hall}} = \alpha/e|R_H|$, where α (the coherence factor) is assumed to be unity. However, the Hall effect data should be carefully assessed in the case of organic semiconductors, in which hopping and band carriers often coexist. Although hopping carriers do not experience a Lorentz force because their net drift velocity is zero, they can be affected by the electric field that is generated via the Hall effect for band carriers, and thus are likely to contribute to the measured Hall voltage.⁴⁴ In a scenario such as this involving a mixed transport regime, α often deviates from unity. In a two-channel conduction model including hopping and band carriers, α is expressed as

$$\alpha = \frac{n}{n_{\text{Hall}}} = \frac{\gamma}{(\gamma - \gamma\beta + \beta)^2}, \quad (21)$$

where n is the total carrier concentration, γ is the ratio of the band carrier concentration to the total carrier concentration, and β is the ratio of the hopping mobility to the band mobility. Note that α is able to take any positive value, and that when $\alpha < 1$ the Hall effect measurements overestimate the actual carrier concentration ($n_{\text{Hall}} > n$) and *vice versa*. Because the total carrier concentration (*i.e.*, the sum of the hopping and band carrier populations) was not determined for the present anion exchanged system, some uncertainty regarding the Hall carrier density is unavoidable in our analysis. However, we emphasize that the Hall carrier density presented in the main text can be considered to represent the lower limit of the actual carrier concentration. From previous studies of the Hall effect in chemically doped PBTTT thin films, the total carrier concentration, n , was determined by spin counting of the anionic dopant, because conventional molecular dopants are free radical anions that purely contribute to the Curie spin paramagnetic susceptibility. The resulting values for the conductivity, σ , the total carrier concentration, n , the Hall carrier density, n_{Hall} , and the coherence factor, α , are summarized in Supplementary Table 10. These data show that the Hall carrier density is likely to be underestimated by a factor of α . Importantly, for highly doped PBTTT specimens, α has a value of approximately 2, which suggests that the present Hall effect measurements for anion exchange doped PBTTT give the lower limit of the total carrier concentration ($n > n_{\text{Hall}}$).

Dopants	σ (S cm ⁻¹)	n (10 ²⁰ cm ⁻³)	n_{Hall} (10 ²⁰ cm ⁻³)	α	μ_{Hall} (cm ² V ⁻¹ s ⁻¹)
F4TCNQ	120	4.1	2.4	1.7	1.8
Mo(tfd-COCF ₃) ₃)	180	8.0	4.0	2.0	2.3
EMIM-TFSI	340	N.A.	8.8	N.A.	1.9
Li-TFSI	440	N.A.	14	N.A.	2.5

Supplementary Table 10: Estimation of the coherence factor. Literature values for the conductivity, σ , the total carrier concentration, n , the Hall carrier density, n_{Hall} , and the coherence factor, α , at room temperature.²⁹

We turn discussions to charge transport mechanism in highly doped, semicrystalline polymers, in particular, the counter-anion effects on carrier scattering. In the ref,⁴⁵ it has been reported that work function (WF) in triphenylamine-based polymers can be tuned precisely by selecting counter anions via Coulomb interaction. The present anion exchange doping

allows a systematic investigation of the counter-anion effects on the Hall mobility. The counter-anion effect on the Hall mobility is summarized in Supplementary Table 10. Judging from previous studies of the Hall effect measurements in highly-doped PBTTT thin films, no apparent relation between counter-anion and the Hall mobility is found. Unlike triphenylamine-based polymers,⁴⁵ in which carriers are localized strongly on nitrogen site of the triphenylamine core, carriers in the highly-doped PBTTT thin film are delocalized across the two-dimensional π -conjugated backbone. Because the delocalization of carriers yields an effective screening of electrostatic potential, the counter-anion effect specifically on the present PBTTT can be minimized. We emphasize again that the observation of the Hall effect is a manifestation of the coherent band transport, where the drift mobility is described as $\mu = \frac{e\tau}{m^*}$ (τ : relaxation time, and m^* : the effective mass). In a heavily-doped Si, a periodic ionized impurity potential is known to cause the ionized impurity scattering, which affects τ .⁴⁶ The dopant effect on electronic conduction in conducting polymers will be of great interest, and it can be addressed by carefully ascertaining temperature dependence of the Hall mobility.

In PBTTT, the field-effect mobility has been reported to be up to $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas the Hall mobility obtained for doped state is $1 \sim 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This increase of mobility can be explained by trap filling effect, *i.e.*, localized trap density-of-states can be filled by doping. When the Fermi level shift close to the valence band edge (corresponding to the HOMO level), charge carriers undergo band transport, which is clearly demonstrated by observing the Hall effect in this work. Given the assumption that the rigid band approximation holds in doped state and the effective mass for transport in the π -stack direction is $0.3 m_0$, the mobility reaches $15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁴⁷ Because there are still many of trap density-of-states in the present doped PBTTT likely due to an unavoidable structural disorder in polymeric semiconductors, the drift mobility may be limited by the contribution of hopping conduction. We emphasize that the present highly-doped state together with band transport in polymeric semiconductors could provide a better platform for in-depth understanding of charge transport physics, and future work is needed to clarify the structure-transport relation in conjugated polymers.

Analysis of positive magnetoconductance. As discussed in the main text, magnetoconductance was observed in response to magnetic fields in the out-of-plane direction relative to the doped films. Positive magnetoconductance is assigned to weak localization in a two-dimensional electron system^{28,29} due to coherent backscattering. Such increases in conductivity in response to a magnetic field appear when the constructive interference between electron waves that traverse closed paths in opposite loops is disrupted by the magnetic field, and is well described by the Hikami-Larkin-Nagaoka (HLN) model.⁴⁸ The full HLN expression is

$$\Delta\sigma(B) = -\frac{e^2}{2\pi^2\hbar}[\Psi(\frac{1}{2} + \frac{B_1}{B}) - \Psi(\frac{1}{2} + \frac{B_2}{B}) + \frac{1}{2}\Psi(\frac{1}{2} + \frac{B_3}{B}) - \frac{1}{2}\Psi(\frac{1}{2} + \frac{B_4}{B})], \quad (22)$$

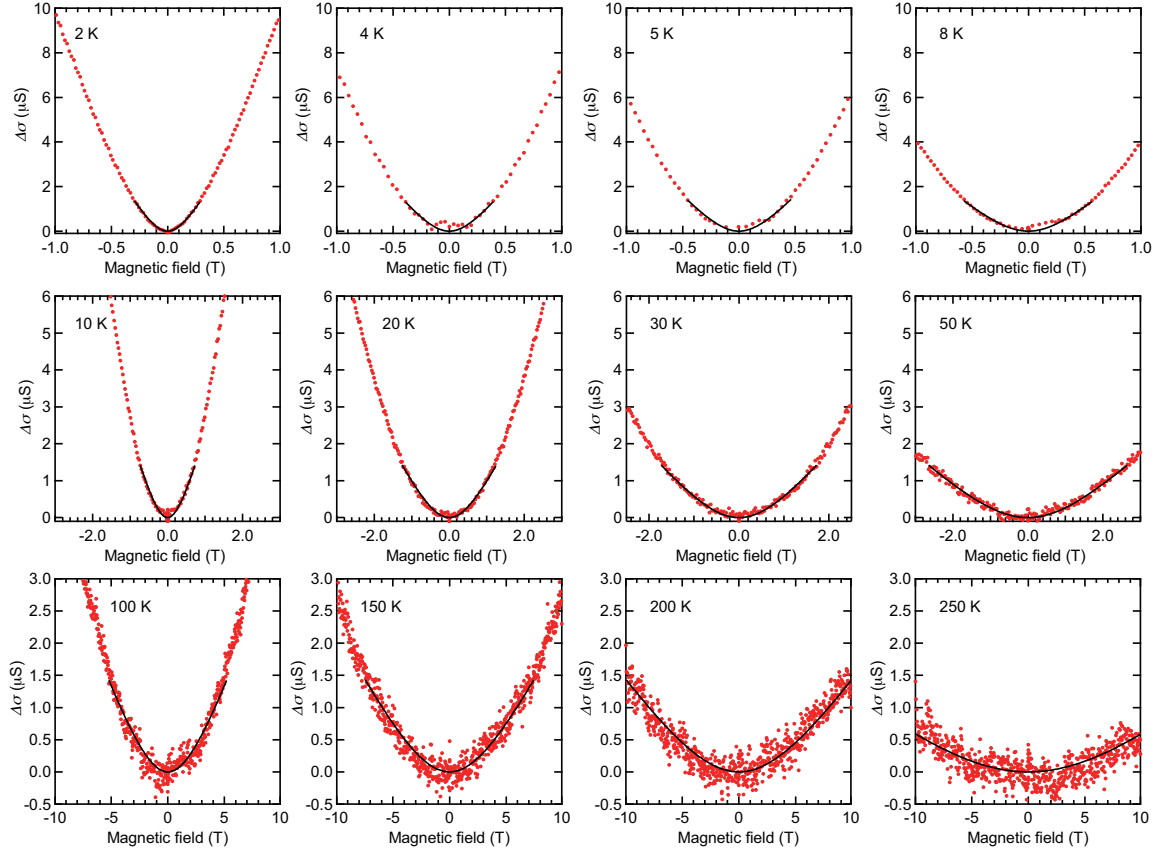
where the prefactor, $e^2/2\pi^2\hbar$, is the quantized conductivity and Ψ is the digamma function. Here, the B_n terms are linear combinations of the characteristic magnetic fields, B_i , and can be written as

$$\begin{aligned} B_1 &= B_e + B_{so} + B_m \\ B_2 &= \frac{4}{3}B_{so} + \frac{2}{3}B_m + B_\phi \\ B_3 &= 2B_{so} + B_\phi \\ B_4 &= \frac{2}{3}B_{so} + \frac{4}{3}B_m + B_\phi \end{aligned}$$

The index, i , denotes different scattering processes: e for elastic scattering, φ for inelastic scattering, so , for spin-orbit scattering, and m for magnetic scattering. Both B_{so} and B_m are expected to be negligible in the case of the doped polymers assessed in this work. Hence, Eq. (17) simplifies to

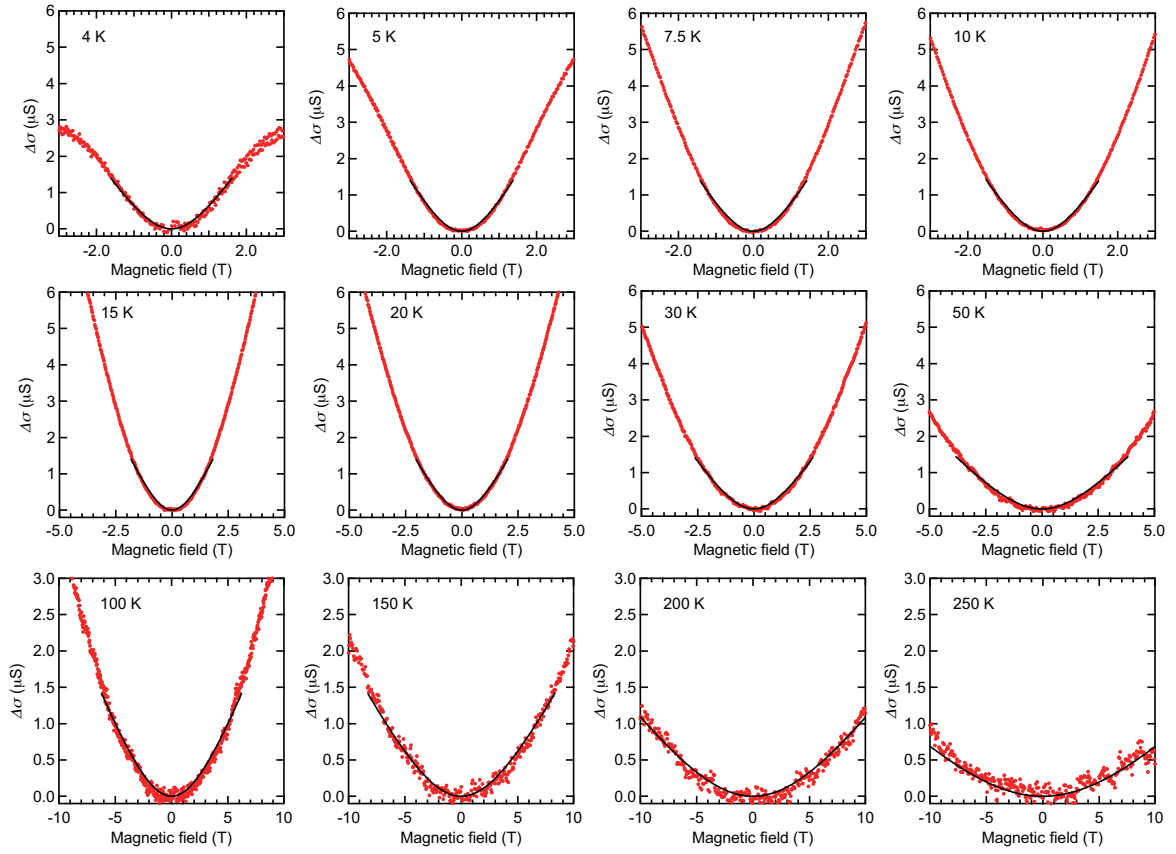
$$\Delta\sigma(B) = -\frac{e^2}{2\pi^2\hbar}[\Psi(\frac{1}{2} + \frac{B_e}{B}) - \Psi(\frac{1}{2} + \frac{B_\phi}{B})]. \quad (23)$$

The phase coherence length, λ_ϕ , can be estimated by fitting the magnetoconductance data based on the HLN equation. In our study, the digamma function²⁸ could not be approximated by a parabolic function of B^2 because B_ϕ was comparable to or smaller than the applied magnetic fields. The Li-TFSI exchanged film exhibited decreased magnetoconductance at high magnetic fields and at low temperatures, suggesting negative magnetoconductance



Supplementary Figure 9: Fitting of magnetoconductance data using the HLN model for the sample anion exchange doped with EMIM-TFSI. Red plots show experimental data and black lines show fitting curves. Temperatures are indicated.

resulting from electron-electron interactions.^{42,49} This appearance of magnetoconductance only at low magnetic fields is primarily attributed to weak localization. As shown in Figs. 9 and 10, the magnetoconductance data were well fit at all temperatures.



Supplementary Figure 10: Fitting of magnetoconductance data using the HLN model for the sample anion exchange doped with EMIM-TFSI. Red plots show experimental data and black lines show fitting curves. Temperatures are indicated.

1.8 Thermal durability of doped thin films

In the main text, the thermal stability and durability of doped PBTTT thin films were presented. Here, in this section, we show more details of measurements and interpretation of thermal stress test. Specimens were subjected to a series of annealing cycles in an Ar-purged glove box after which absorption spectra were acquired in air. In this process, the annealing temperature was raised for each cycle to a maximum of 160 °C, which is below the glass transition temperature of PBTTT (180 °C). Extended Data Fig. 10 in the main text presents the spectra obtained from thin films doped with F4TCNQ and anion exchange doped with various salts. The F4TCNQ-doped PBTTT loses the doping effect at an annealing temperature of 160 °C, as confirmed by the disappearance of the broad tail above 1500 nm. this loss of doping is attributed to the evaporation of the F4TCNQ following charge back-transfer. In contrast, the PBTTT film doped with BOB⁻ does not exhibit this effect, as charge back transfer is not expected due to the closed-shell nature of the BOB⁻ (Extended Data Fig. 10). Loss of the doping effect in the PBTTT films in conjunction with closed-shell anions would be expected to occur only when the anions react with other chemicals, such as a reaction with water to form H-BOB after reduction of the doped PBTTT. Thus, the hydrophobicity and chemical stability of anions are both important aspects of improving thermal durability. The enhanced thermal durability demonstrated herein could lead to new opportunities with regard to realizing organic thermoelectric power generators. Recent developments have resulted in highly efficient thermoelectric converters based on printing technology. However, the operating temperature of the organic thermoelectric elements is generally limited to below 100 °C. The anion exchange doping demonstrated in the present study improves thermal durability while tuning the doping level, both of which could potentially accelerate further developments in organic thermoelectric applications.

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