

Using pre-formed Meisenheimer complexes as dopants for n-type organic thermoelectrics with high Seebeck coefficients and power factors

Jinfeng Han¹, Connor Ganley², Qin Hu^{3,4}, Xingang Zhao¹, Paulette Clancy², Thomas P. Russell^{3,4}, Howard E. Katz¹, *

J. Han, X. Zhao, Prof. H. E. Katz

¹Department of Materials Science and Engineering and Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States.

Email: hekatz@jhu.edu

C. Ganley, Prof. P. Clancy

²Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States.

Q. Hu, Prof. T. P. Russell

³Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, United States

⁴Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Keywords: complex dopant, n-type polymer thermoelectrics, high Seebeck coefficient, high power factor.

Abstract:

A pre-formed Meisenheimer complex of an NDI with TBAF was obtained in a simple way by mixing dibrominated NTCDI and tetrabutylammonium fluoride (TBAF) in solution and used as dopant for n-type organic thermoelectrics. Two *n*-type polymers PNDICITVT and PBDOPVTT were synthesized, *n*-doped, and characterized as conductive and thermoelectric materials. PNDICITVT doped with the NDI-TBAF presents a high σ value of 0.20 S cm⁻¹, a Seebeck Coefficient, *S*, of -1854 μ V K⁻¹ and a power factor (*PF*) of 67 μ W m⁻¹ K⁻², among the highest reported *PF* in solution-

processed conjugated *n*-type polymer thermoelectrics. Using N-DMBI and NDI-TBAF as co-dopants, PNDICITVT has a $PF > 35 \mu\text{W m}^{-1} \text{K}^{-2}$; while for PBDOPVTT $\sigma = 0.75 \text{ S cm}^{-1}$ and $PF = 58 \mu\text{W m}^{-1} \text{K}^{-2}$. In this work, we found that an ionic adduct together with a neutral dopant improved the performance of *n*-type organic thermoelectrics leading to an enhanced power factor, and elucidated the role of such an adduct more generally in polymer doping.

Introduction:

Organic semiconducting materials have found a broad range of applications, including commercially, as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs) and photovoltaic devices.^[1] Dopants at low concentrations have been shown to improve semiconductor performance in such devices,^[2] for example by promoting charge injection into OLEDs and filling traps to increase mobility in OFETs, as will be discussed below. There is also renewed and increasing interest in the design of conjugated polymer-dopant systems to produce printable, flexible, optoelectronic, and bio-active electronic conductors.^[3] Organic conductors are also attracting increased attention for low-temperature thermoelectric applications.^[4] Conjugated polymers offer a number of advantages in that they are lightweight, and solution processable, and have low thermal conductivity, an improved low-temperature thermoelectric performance (<200 °C), and a natural mechanical flexibility. As a result, conjugated polymers are promising materials for current and near future wearable electronics.^[5]

The power factor, PF , is usually used to assess the thermoelectric performance. It can be calculated from following equation:

$$PF = S^2 \sigma \quad [1]$$

where S is the Seebeck coefficient ($\mu\text{V K}^{-1}$), σ is the electrical conductivity (S cm^{-1}). Because conjugated polymers generally have similar values of thermal conductivity, improving the electrical conductivity and Seebeck coefficient will effectively enhance thermoelectric performance. The electrical conductivity of the most conductive p -type polymers is on the order of hundreds to thousands of S cm^{-1} , and the power factor is usually tens to hundreds of $\mu\text{W/m K}^2$.^[4a, 6] Compared to p -type organic thermoelectric materials, n -type organic thermoelectric materials usually exhibit lower values of σ and S , resulting in lower ZT and PF .

Several approaches have been explored to improve the power factor of n -type organic thermoelectrics. Huang *et al.* developed a quinoid molecule with a high PF of $236 \mu\text{W m}^{-1} \text{K}^{-2}$ at 373 K , demonstrating a powerful strategy to achieve high performance organic thermoelectrics.^[7] For n -type polymer thermoelectrics backbone engineering is an effective way to improve σ or S . Lei and coworkers designed and synthesized a pyrazine-flanked DPP-based polymer, with a short π - π stacking distance of 3.38 \AA , that presented a high PF of $57 \mu\text{W m}^{-1} \text{K}^{-2}$.^[8] These studies typically used 4-(1,3-Dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl)dimethylamine (N-DMBI) as the dopant, and the polymer synthesis process is not straightforward. Most n -type

polymer thermoelectrics have PF values below $30 \mu\text{W m}^{-1} \text{K}^{-2}$ and breakthroughs are difficult to achieve.^[5a, 9] This provides an incentive to introduce novel n -type dopants to meet the demand of improved electron transport in organic semiconducting films.^[10] Previously, we used tetrabutylammonium fluoride (TBAF) as a polymer dopant to prepare thermoelectric devices, yielding $\sigma = 0.62 \text{ S cm}^{-1}$.^[11] Pei *et al.* reported a new dopant, triaminomethane (TAM), for n -type polymer thermoelectrics and reported a high PF of $51 \mu\text{W m}^{-1} \text{K}^{-2}$.^[12] Recently, devices with improved electron mobility (up to $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) were achieved by doping N2200 (poly[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)) with an adduct, (12a,18a)-5,6,12,12a,13,18,18a,19-octahydro-5,6-dimethyl-13,18[1',2']-benzenobisbenzimidazo [1,2-b:2',1'-d]benzo[*i*][2.5]benzodiazocine potassium triflate (DMBI-BDZC).^[13]

In some of the examples mentioned above, dopants are used that do not seem to be plausible single-electron acceptors or donors, even though they show dopant activity. Tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) was used with conjugated polymers and their molecular semiconductor blends, not in order to reach a high σ value, but rather to increase the field-effect transistor mobility, possibly by oxidizing traps.^[14] In another case, a substantial σ was achieved in poly(3-hexylthiophene) doped with $\text{B}(\text{C}_6\text{F}_5)_3$.^[15] Kao *et al.* showed that fluoroalkyltrichlorosilanes were extremely effective dopants to make high- σ polythiophenes, but the authors argued that the doping mechanism involved protons generated by hydrolysis of the silanes.^[16] This is consistent with

statements in a recent publication about $(\text{B}(\text{C}_6\text{F}_5)_3)$ that $(\text{B}(\text{C}_6\text{F}_5)_3)$ does not act as an oxidant, but instead reacts with water to form a Brønsted acid, whose proton forms a covalent adduct with a mildly Lewis basic polymer that serves as a dopant for another polymer chain.^[17] Doping by the strong acid bis(trifluoromethanesulfonyl)imide of the sterically hindered poly(3-(2-ethylhexyl)thiophene) was found to be two orders of magnitude better as a dopant than tetrafluorotetracyanoquinodimethane (F_4TCNQ).^[18] Thomas *et al.* stated^[19], “For acidic dopants, it is postulated that the carbocation generated from backbone protonation oxidizes a neighboring chain, leading to the traditional radical-hole pair and the associated Brønsted base.” There are multiple references to the general use of small anions (even F^-) as dopants for fullerenes and other small molecules,^[20] but there is some question as to whether F^- could act as an electron donor,^[21] making it more likely that fluoro-Meisenheimer complexes formed *in situ* from F^- and polymer subunits could be electron donors for other polymer chains.

In this paper, using NTCDI and TBAF as raw materials, we developed the pre-formed Meisenheimer complexes of NDI-TBAF as *n*-type dopant of a dibrominated NDI + TBAF using a simple mixing method. The NMR spectra of NDI-TBAF is shown in supporting information.^[21b] We synthesized a new polymer, PNDICITVT, based on a weak donor unit dichlorodithienylethene (CITVT) by Stille coupling in ortho-dichlorobenzene (*o*-DCB) (**Figure 1a**). PBDOPVTT was synthesized by Stille coupling PNDICITVT in chlorobenzene (**Figure 1a**). The M_w values of PNDICITVT

and PBDOPVTT are 154 and 116 kDa, respectively, and the corresponding polydispersity indices (PDIs) are 3.7 and 1.3. PNDICITVT doped with NDI-TBAF shows a high σ of 0.20 S cm^{-1} , comparable to films doped with N-DMBI, and a much higher S of $-1854 \text{ } \mu\text{V K}^{-1}$. We show that this results in an improved PF of $67 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ (10 wt%), the highest PF in solution-processed conjugated n -type all-polymer thermoelectrics. This is also the first demonstration of a pre-formed Meisenheimer complex showing doping capabilities, supporting the above hypothesis. To improve the performance stability of NDI-TBAF-based devices, N-DMBI and 5 wt% NDI-TBAF as co-dopants, creating a doped polymer that displays a high PF , exceeding $35 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ at the N-DMBI ratio of 30 mol% and 50 mol%. To demonstrate the value of co-dopants to improve performance, we prepared thermoelectric devices based on doped PBDOPVTT, obtaining a high σ of 0.75 S cm^{-1} (50 mol% N-DMBI and 5 wt% NDI-TBAF) and a PF near $60 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ at a N-DMBI ratio of 50 mol% and 75 mol%. To the best of our knowledge, this PF value is one of the highest power factors of n -type donor-acceptor (D-A) polymers (**Figure 1b**),^[8, 9b-e, 11, 22] suggesting an enhancement resulting from co-dopants and the additional advantage in using Meisenheimer complexes for n -type polymer thermoelectrics. We used *ab initio* density functional theory calculations of key molecular structures and their electronic properties to help evaluate the mechanism by which such complexes promote n -type polymer conductivity.

Experimental Results:

NDI-TBAF (mole ratio:1/1) was prepared by mixing NTCDI and TBAF (1 M in THF) in a glove box (N_2 , $H_2O < 6$ ppm, $O_2 < 0.1$ ppm) and made up as a solution in THF with total concentration of 2.5 mg/mL. NDI-TBAF has been studied by Teck Lip Dexter Tam and Jian Wei Xu,^[21b] The color of the NDI-TBAF mixed solution is red, readily distinguishing it from the color of NTCDI (faint yellow) and TBAF (colorless) (Figure s10). The 1H NMR spectra of NDI-TBAF shows that the environment of hydrogen atoms in the NDI are altered by the addition of TBAF.

As described in more detail in the Supporting Information, PNDICITVT was synthesized by coupling NDI-2Br with a weak donor of CITVT. PBDOPVTT is an *n*-type polymer based on dichlorinated BDOPV and bithiophene.^[23] A pristine film of PNDICITVT has a maximal, low-energy absorption peak at 647 nm with a smaller shoulder peak at 712 nm; no obvious absorption was observed beyond 850 nm (**Figure 2a**). PNDICITVT doped with 5 wt% NDI-TBAF presents stronger absorption than the pristine polymer film and the absorption spectra can be detected beyond 850 nm, suggesting PNDICITVT can be successfully *n*-doped by NDI-TBAF. When the ratio of NDI-TBAF was increased to 10 wt%, the absorption at 550-750 nm is much stronger than that doped with 5 wt%; however, absorption beyond 850 nm is weaker (**Figure 2a**). The two absorption peaks between 600 nm and 750 nm became a single broad peak when PNDICITVT was doped with 5 wt% NDI-TBAF and 30 mol% N-DMBI. When N-DMBI was increased to 100 mol%, the absorption spectra beyond that region is much stronger than that doped with 30 mol% N-DMBI (**Figure 2a**).

PBDOPVTT doped with NDI-TBAF has weaker polaron absorption than PNDICITVT, suggesting that PNDICITVT can be more easily doped by NDI-TBAF (**Figure 2b**). The LUMO energy levels of PNDICITVT and PBDOPVTT are similar, ~ -3.90 eV, and the HOMO energy level of PBDOPVTT (-5.55 eV) is slightly lower than that of PNDICITVT (-5.47 eV). The LUMO and HOMO energy levels of PNDICITVT and PBDOPVTT doped with 5 wt% NDI-TBAF are $-3.81/-5.54$ eV and $-3.91/-5.50$ eV, respectively. This shows little change, especially for PBDOPVTT (**Figure 2c, d**). The result also shows that PNDICITVT can be more easily doped by NDI-TBAF than can PBDOPVTT. The EPR spectra of intrinsic and doped PNDICITVT and PBDOPVTT indicate that both of them can be doped by the preassembled complex (**Figure 2e and 2f**).

We measured the thermoelectric properties of doped polymers in the open air. The thickness of polymer films is about 300-400 nm, the doped polymer films are stable during measurement process. PNDICITVT doped with 10 wt% NDI-TBAF showed a maximum conductivity of 0.20 S cm^{-1} (**Figure 3a**). This result shows an enhancement in the conductivity from 0.006 to 0.2 S cm^{-1} as the NDI-TBAF ratio was increased from 0.5 wt% to 10 wt% (**Figure 3a**). Due to the negative correlation between the Seebeck coefficient and charge carrier concentration, the corresponding Seebeck coefficient decreased from -3900 to $-1850 \mu\text{V K}^{-1}$ (**Figure 3d**). The PF value improved from $9.2 \mu\text{W m}^{-1} \text{ K}^{-2}$ (0.5 wt%) to $67 \mu\text{W m}^{-1} \text{ K}^{-2}$ (10 wt%), which is among the highest power factors yet observed in *n*-type solution-processed conjugated polymer

thermoelectrics (**Figure 1a and 3d**). It is possible that the high Seebeck coefficient could include an ionic thermogalvanic, or energy filtering contribution,^[24] as discussed below. N-DMBI, which was developed by the Bao group, can promote hydrogen- and/or electron-transfer reactions via radical formation and is known to play a key role in recent *n*-type organic thermoelectrics.^[25] A maximum value of $\sigma = 0.11 \text{ S cm}^{-1}$ was obtained when PNDICITVT was doped with 50 mol% N-DMBI (**Figure 3b**). When the N-DMBI ratio increased from 5 mol% to 75 mol%, the Seebeck coefficient of doped PNDICITVT decreased from -770 to $-310 \mu\text{V K}^{-1}$ (**Figure 3e**). If the N-DMBI ratio is increased to 100 mol%, S became positive, producing a value of $146 \mu\text{V K}^{-1}$. The S value of PNDICITVT doped with N-DMBI is far below that doped with NDI-TBAF and their σ is close, resulting in a much lower PF of $2.6 \mu\text{W m}^{-1} \text{ K}^{-2}$ (**Figure 3e**).

Though the maximum value for the PF of PNDICITVT doped with NDI-TBAF is very high, we found that its performance was not very consistent, perhaps due to an transistor contribution to the Seebeck coefficient. To decrease this possibility, we created thermoelectric devices with 5 wt% NDI-TBAF and various fractions of N-DMBI as co-dopants. When the N-DMBI ratio is 75 mol%, doped PNDICITVT exhibited the maximum σ of 0.12 S cm^{-1} ; even when the N-DMBI ratio was reduced to 50 mol%, the σ remains close to 0.10 S cm^{-1} , suggesting that high σ values can be obtained in a broader range of N-DMBI fraction than when N-DMBI is the sole dopant (**Figure 3c**). The Seebeck coefficient decreased from -7200 to $-850 \mu\text{V K}^{-1}$ when the N-DMBI ratio increased from 5 mol% to 100 mol% (**Figure 3f**). When the

N-DMBI ratio is 50 mol%, doped PNDICITVT presented the highest PF of $36 \mu\text{W m}^{-1} \text{K}^{-2}$ (**Figure 3f**). Moreover, both PNDICITVT:5 wt% NDI-TBAF doped with 50 mol% and 75 mol% showed high PF values above $35 \mu\text{W m}^{-1} \text{K}^{-2}$, which is much higher than that doped with a single dopant of N-DMBI, showing the enhancement in performance due to the use of co-dopants (**Figure 3f**).

PBDOPVTT doped with NDI-TBAF presented the best σ of 0.04 S cm^{-1} at a dopant weight ratio of 10 wt%, with corresponding values for S and PF of $-1640 \mu\text{V K}^{-1}$ and $8.3 \mu\text{W m}^{-1} \text{K}^{-2}$, respectively (**Figure 4a, d**). The highest PF is $9.5 \mu\text{W m}^{-1} \text{K}^{-2}$ (5 wt%) due to the correspondingly high value of S of $-5216 \mu\text{V K}^{-1}$ (**Figure 4d**). The best σ of PBDOPVTT doped with N-DMBI is 8.1 S cm^{-1} (75 mol%) and the corresponding PF is $21 \mu\text{W m}^{-1} \text{K}^{-2}$ (**Figure 4b, e**), which is similar to that reported for other N-DMBI-doped n -type conjugated polymers.^[9d, 22c] Using 5 wt% NDI-TBAF and varying the fraction of N-DMBI as co-dopants, we were able to create doped PBDOPVTT with a σ of 0.75 S cm^{-1} (50 mol% N-DMBI), and corresponding S and PF values of $-870 \mu\text{V K}^{-1}$ and $56 \mu\text{W m}^{-1} \text{K}^{-2}$, respectively (**Figure 4c, f**). The highest PF was $58 \mu\text{W m}^{-1} \text{K}^{-2}$ (75 mol% N-DMBI), which arises from a higher S value of $-960 \mu\text{V K}^{-1}$. The PF is higher than that of previously reported n -type conjugated polymer thermoelectrics, suggesting the generality of using co-dopants to achieve high power factor n -type polymer thermoelectrics.

According to previous reports, σ follows an Arrhenius-type dependence of

conductivity with temperature T , which can be determined by the equation:

$$\sigma_e = \sigma_{e, \infty} \exp\left(\frac{-E_A}{k_B T}\right) \quad (2)$$

where $\sigma_{e, \infty}$ is the theoretical maximal electrical conductivity, k_B is Boltzmann constant, T is temperature and E_A are the thermal activation energy.^[26] To understand σ at different temperatures, σ of PNDICITVT and PBDOPVTT doped with co-dopants at about -10-260°C (average of about 400 K) was measured. Both polymers exhibit linear \ln conductivity-reciprocal temperature dependence (**Figure 5**). The thermal activation energy of carrier hopping is calculated to be 154 and 81 meV for PNDICITVT and PBDOPVTT, respectively. Dividing by 400 K yields a projected S of 200-400 $\mu\text{V/K}$, several times less than what was measured for the highest PF samples, indicating a contribution from an alternate mechanism such as ionic redistribution, a thermogalvanic effect, or energy filtering. It should be noted that the electroactivities of fluoride and TBA ions are minimal, making a thermogalvanic effect based on those species unlikely.

The electron mobility of pristine PNDICITVT and PBDOPVTT was evaluated to be 0.05 ± 0.01 and $0.09 \pm 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively; the on/off ratio of two polymers is about 2000 (Figure s2). The electron mobilities of PNDICITVT and PBDOPVTT doped with 0.05 wt% NDI-TBAF are 0.03 and 0.04 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, and the threshold voltage is much lower than that of pristine polymers (Figure s3a and s4a). This may be because the ions in THF can disorder the molecular packing of polymer films. The electron mobilities of PNDICITVT and PBDOPVTT doped with 0.02 mol

% N-DMBI are enhanced to be 0.09 and 0.4 cm² V⁻¹ s⁻¹, respectively, which are much higher than that of the pristine polymers, especially for PBDOPVTT (Figure s3b and s4b). Using 0.05 wt% NDI-TBAF and 0.02mol% N-DMBI as the co-dopants, electron mobility of 0.1 and 0.8 cm² V⁻¹ s⁻¹ were obtained for PNDICITVT and PBDOPVTT (Figure s3c and s4c), respectively, and they are higher than those of pristine polymers, doped with N-DMBI or doped with NDI-TBAF, showing the excellent performance of co-dopants.

Grazing incidence wide angle X-ray scattering shows that PBDOPVTT is more crystalline in pristine film. The pristine PBDOPVTT presents an edge-on orientation, and PNDICITVT presents both edge-on and face-on orientations. The lamellar packing and π - π stacking distances were calculated to be 25.1 Å ($q = 0.251 \text{ \AA}^{-1}$) and 3.63 Å ($q = 1.73 \text{ \AA}^{-1}$) for PNDICITVT and 31.4 ($q = 0.2 \text{ \AA}^{-1}$) and 3.45 Å ($q = 1.82 \text{ \AA}^{-1}$) for PBDOPVTT (Figure s5). PNDICITVT and PBDOPVTT doped with NDI-TBAF showed a higher degree of face-on π - π stacking than the pristine polymers, especially for PBDOPVTT, the π - π stacking distances were 3.59 Å ($q = 1.75 \text{ \AA}^{-1}$) and 3.49 Å ($q = 1.8 \text{ \AA}^{-1}$), respectively (Figure s5). Both PNDICITVT and PBDOPVTT doped with co-dopants have much weaker π - π stacking diffraction intensity, suggesting that the two different dopants may disorder the arrangement of molecules (**Figure 6b**). Atomic force microscope (AFM) images suggest that PNDICITVT doped with NDI-TBAF or N-DMBI are miscible, perhaps related to the fact that that films of PNDICITVT doped with NDI-TBAF, N-DMBI and co-dopants all have similar electrical conductivity

(Figure s6). However, PBDOPVTT doped with N-DMBI shows better miscibility than that doped with NDI-TBAF or co-dopants (Figure s7). If we can improve the miscibility of PBDOPVTT doped with NDI-TBAF, a higher conductivity might be achieved.

Computational Results:

To evaluate the possible role of adduct dopants in the electronic property enhancements described above, we simulated the electronic structures and calculated ionization potentials of representative dopant structures using density functional theory (DFT). We used the ORCA software package^[27] to model the components of the adduct and represented the acetonitrile as an “implicit solvent” (expressed as a mean field of a suitable dielectric constant). Details of the DFT methodology, parameters, and settings used in this computational investigation are provided in the Supporting Information. We uncovered three energetically preferred sites of complexation of a bare fluoride ion to the N,N-dimethyl NDI were uncovered in our initial studies of a simplified system (**Figure 6**), with the strongest binding energy to the carbonyl carbons at around 0.2 eV. When we incorporated tetramethylammonium as a counterion in separate simulations, the binding energy increased to about 0.6 eV, *i.e.*, became stronger, and the ionization energy of the adduct with its counterion is calculated to be about 6.3 eV. Use of Cs⁺ as a counterion gave a similar ionization energy, although -interestingly- it showed essentially no binding energy (comparable to that of the bare fluoride adduct complex), consistent with unsuccessful attempt to

observe that adduct by NMR. We also found that both the binding energy and ionization energy of the counterion systems were isotropic with respect to the counterion's position around the fluoride ion. The ionization energy is about 2 eV less than the likely electron affinities of the *n*-type polymers used in this paper, but those affinities do not account for the presence of the counterions, or the increased entropy resulting from the many more possible electronic configurations of doped polymers compared to the adducts. Most importantly, the ionization energies of tetramethylammonium and cesium fluorides are calculated to be 7.2 and 7.6 eV, respectively, a full eV higher than that of the adduct, making the adduct a much more likely source of *n*-doping than the pure fluoride salts. Also, the binding energy is considerably higher than the activation for mobility, making fluoride transport an unlikely mechanism for the change in conductivity.

Conclusions:

We used pre-formed Meisenheimer complexes of NDI-TBAF as *n*-type dopants and showed their utility in achieving high Seebeck coefficient- and power factor *n*-type polymer thermoelectrics. PNDICITVT doped with NDI-TBAF presents a high power factor of $67 \mu\text{W m}^{-1} \text{K}^{-2}$. Using N-DMBI and NDI-TBAF as co-dopants, *PF* of 36 and $58 \mu\text{W m}^{-1} \text{K}^{-2}$ were achieved for PNDICITVT and PBDOPVTT, respectively. Our results showed, for the first time, that F⁻ incorporated as a Meisenheimer adduct, the form in which it may generally be present in *n*-type polymers, is active as an *n*-dopant and that this type of dopant can be used for high performance *n*-type organic

thermoelectrics, including as a co-dopant with N-DMBI.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

Acknowledgements

We thank Professor Patricia McGuiggan for assistance with AFM measurements. We also thank Dr. Tushita Mukhopadhyaya (Howard E. Katz group) and Garvin Peters (J.D. Tovar group) for their assistance with CV measurements, Arlene Chiu (Susanna Thon's group) for her help with UV-vis-NIR spectra measurements, and Baixiang Li for his help with GPC measurements. This work was primarily supported by the National Science Foundation, Division of Chemistry, grant number 1708245. Q. Hu and T. P. Russell were supported by the US Office of Naval Research under contract N00014-17-1-2241. GIWAXS were performed at beamline 7.3.3 of the Advanced Light Source, Lawrence Berkeley National Laboratory, which is supported by the DOE, Office of Science, and Office of Basic Energy Sciences.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References:

- [1] a) S. Yuvaraja, A. Nawaz, Q. Liu, D. Dubal, S. G. Surya, K. N. Salama, P. Sonar, *Chemical Society Reviews* **2020**, *49*, 3423; b) A. Wadsworth, Z. Hamid, J. Kosco, N. Gasparini, I. McCulloch, *Adv. Mater.* **2020**, *32*, 2001763; c) S. Wang, H. Zhang, B. Zhang, Z. Xie, W.-Y. Wong, *Materials Science and Engineering: R: Reports* **2020**, *140*, 100547; d) S.-J. Zou, Y. Shen, F.-M. Xie, J.-D. Chen, Y.-Q. Li, J.-X. Tang, *Materials Chemistry Frontiers* **2020**, *4*, 788.
- [2] B. Lüssem, M. Riede, K. Leo, *Phys. Status Solidi (a)* **2013**, *210*, 9.
- [3] a) M. Bharti, A. Singh, S. Samanta, D. K. Aswal, *Prog. Mater.Sci.* **2018**, *93*, 270; b) C. J. Yao, H. L. Zhang, Q. Zhang, *Polymers (Basel)* **2019**, *11*; c) S. Inal, J. Rivnay, A. O. Suiu, G. G. Malliaras, I. McCulloch, *Acc. Chem. Res.* **2018**, *51*, 1368; d) J. Liu, Y. Shi, J. Dong, M. I. Nugraha, X. Qiu, M. Su, R. C. Chiechi, D. Baran, G. Portale, X. Guo, L. J. A. Koster, *ACS Energy Lett.* **2019**, *4*, 1556; e) M. Moser, J. F. Ponder, A.

- Wadsworth, A. Giovannitti, I. McCulloch, *Adv. Funct. Mater.* **2018**, *29*.
- [4] a) O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, X. Crispin, *Nat. Mater.* **2011**, *10*, 429; b) B. Russ, A. Glauddell, J. J. Urban, M. L. Chabinyk, R. A. Segalman, *Nat. Rev. Mater.* **2016**, *1*; c) S. Lee, S. Kim, A. Pathak, A. Tripathi, T. Qiao, Y. Lee, H. Lee, H. Y. Woo, *Macromolecular Research* **2020**, *28*, 531; d) M. Lindorf, K. A. Mazzio, J. Pflaum, K. Nielsch, W. Brütting, M. Albrecht, *Journal of Materials Chemistry A* **2020**, *8*, 7495.
- [5] a) R. M. Kluge, N. Saxena, W. Chen, V. Körstgens, M. Schwartzkopf, Q. Zhong, S. V. Roth, P. Müller-Buschbaum, *Adv. Funct. Mater.* **2020**, 2003092; b) T. Park, C. Park, B. Kim, H. Shin, E. Kim, *Energy Environ. Sci.* **2013**, *6*; c) S. Panigrahy, B. Kandasubramanian, *Eur. Polym. J.* **2020**, *132*; d) P. C. Y. Chow, T. Someya, *Adv. Mater.* **2020**, *32*, 1902045; e) W. Shi, Y. Guo, Y. Liu, *Adv. Mater.* **2020**, *32*, 1901493; f) M. Wang, P. Baek, A. Akbarinejad, D. Barker, J. Travas-Sejdic, *Journal of Materials Chemistry C* **2019**, *7*, 5534.
- [6] Y. Du, K. F. Cai, S. Chen, P. Cizek, T. Lin, *ACS Appl. Mater. Inter.* **2014**, *6*, 5735.
- [7] D. Huang, H. Yao, Y. Cui, Y. Zou, F. Zhang, C. Wang, H. Shen, W. Jin, J. Zhu, Y. Diao, W. Xu, C. A. Di, D. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 13013.
- [8] X. Yan, M. Xiong, J. T. Li, S. Zhang, Z. Ahmad, Y. Lu, Z. Y. Wang, Z. F. Yao, J. Y. Wang, X. Gu, T. Lei, *J. Am. Chem. Soc.* **2019**, *141*, 20215.
- [9] a) S. Wang, H. Sun, T. Erdmann, G. Wang, D. Fazzi, U. Lappan, Y. Puttisong, Z. Chen, M. Berggren, X. Crispin, A. Kiriy, B. Voit, T. J. Marks, S. Fabiano, A. Facchetti, *Adv. Mater.* **2018**, *30*, e1801898; b) J. Liu, G. Ye, B. V. Zee, J. Dong, X. Qiu, Y. Liu, G. Portale, R. C. Chiechi, L. J. A. Koster, *Adv. Mater.* **2018**, *30*, e1804290; c) C. Y. Yang, W. L. Jin, J. Wang, Y. F. Ding, S. Nong, K. Shi, Y. Lu, Y. Z. Dai, F. D. Zhuang, T. Lei, C. A. Di, D. Zhu, J. Y. Wang, J. Pei, *Adv. Mater.* **2018**, *30*, e1802850; d) K. Shi, F. Zhang, C. A. Di, T. W. Yan, Y. Zou, X. Zhou, D. Zhu, J. Y. Wang, J. Pei, *J. Am. Chem. Soc.* **2015**, *137*, 6979; e) S. Wang, H. Sun, U. Ail, M. Vagin, P. O. Persson, J. W. Andreasen, W. Thiel, M. Berggren, X. Crispin, D. Fazzi, S. Fabiano, *Adv. Mater.* **2016**, *28*, 10764; f) O. Bardagot, P. Kubik, T. Marszalek, P. Veyre, A. A. Medjahed, M. Sandroni, B. Grévin, S. Pouget, T. Nunes Domschke, A. Carella, S. Gambarelli, W. Pisula, R. Demadrille, *Adv. Funct. Mater.* **2020**, *30*, 2000449.
- [10] D. Huang, C. Wang, Y. Zou, X. Shen, Y. Zang, H. Shen, X. Gao, Y. Yi, W. Xu, C. A. Di, D. Zhu, *Angew Chem. Int. Ed.* **2016**, *55*, 10672.
- [11] X. Zhao, D. Madan, Y. Cheng, J. Zhou, H. Li, S. M. Thon, A. E. Bragg, M. E. DeCoster, P. E. Hopkins, H. E. Katz, *Adv. Mater.* **2017**, *29*.
- [12] C. Y. Yang, Y. F. Ding, D. Huang, J. Wang, Z. F. Yao, C. X. Huang, Y. Lu, H. I. Un, F. D. Zhuang, J. H. Dou, C. A. Di, D. Zhu, J. Y. Wang, T. Lei, J. Pei, *Nat. Commun.* **2020**, *11*, 3292.
- [13] J. Panidi, J. Kainth, A. F. Paterson, S. Wang, L. Tsetseris, A. H. Emwas, M. A. McLachlan, M. Heeney, T. D. Anthopoulos, *Adv. Funct. Mater.* **2019**, *29*, 1902784.
- [14] a) Y. Han, G. Barnes, Y.-H. Lin, J. Martin, M. Al-Hashimi, S. Y. AlQaradawi, T. D. Anthopoulos, M. Heeney, *Chem. Mater.* **2016**, *28*, 8016; b) J. Panidi, A. F. Paterson, D. Khim, Z. Fei, Y. Han, L. Tsetseris, G. Vourlias, P. A. Patsalas, M.

Heeney, T. D. Anthopoulos, *Adv. Sci.* **2018**, *5*, 1700290.

[15] P. Pingel, M. Arvind, L. Kölln, R. Steyrleuthner, F. Kraffert, J. Behrends, S. Janietz, D. Neher, *Adv. Electron. Mater.* **2016**, *2*.

[16] C. Y. Kao, B. Lee, L. S. Wielunski, M. Heeney, I. McCulloch, E. Garfunkel, L. C. Feldman, V. Podzorov, *Adv. Funct. Mater.* **2009**, *19*, 1906.

[17] B. Yurash, D. X. Cao, V. V. Brus, D. Leifert, M. Wang, A. Dixon, M. Seifrid, A. E. Mansour, D. Lungwitz, T. Liu, P. J. Santiago, K. R. Graham, N. Koch, G. C. Bazan, T. Q. Nguyen, *Nat. Mater.* **2019**, *18*, 1327.

[18] E. M. Thomas, E. C. Davidson, R. Katsumata, R. A. Segalman, M. L. Chabinyc, *ACS Macro Lett.* **2018**, *7*, 1492.

[19] C. C. Han, Elsenbaumer, R. L., *Synthetic Met.* **1989**, *30*, 123.

[20] a) C. Z. Li, C. C. Chueh, F. Ding, H. L. Yip, P. W. Liang, X. Li, A. K. Jen, *Adv. Mater.* **2013**, *25*, 4425; b) S. Torabi, J. Liu, P. Gordiichuk, A. Herrmann, L. Qiu, F. Jahani, J. C. Hummelen, L. J. Koster, *ACS Appl. Mater. Inter.* **2016**, *8*, 22623.

[21] a) C. D. Weber, C. Bradley, M. C. Lonergan, *J. Mater. Chem. A* **2014**, *2*, 303; b) T. L. D. Tam, J. W. Xu, *Chem. Commun.* **2019**, *55*, 6225.

[22] a) R. A. Schlitz, F. G. Brunetti, A. M. Glauddell, P. L. Miller, M. A. Brady, C. J. Takacs, C. J. Hawker, M. L. Chabinyc, *Adv. Mater.* **2014**, *26*, 2825; b) S. Hwang, W. J. Potscavage, Y. S. Yang, I. S. Park, T. Matsushima, C. Adachi, *Physical Chemistry Chemical Physics* **2016**, *18*, 29199; c) W. Ma, K. Shi, Y. Wu, Z. Y. Lu, H. Y. Liu, J. Y. Wang, J. Pei, *ACS Appl. Mater. Inter.* **2016**, *8*, 24737; d) Y. Wang, K. Takimiya, *Adv. Mater.* **2020**, *32*, 2002060; e) C.-Y. Yang, Y.-F. Ding, D. Huang, J. Wang, Z.-F. Yao, C.-X. Huang, Y. Lu, H.-I. Un, F.-D. Zhuang, J.-H. Dou, C.-a. Di, D. Zhu, J.-Y. Wang, T. Lei, J. Pei, *Nature Communications* **2020**, *11*, 3292.

[23] Y.-Q. Zheng, Z.-F. Yao, T. Lei, J.-H. Dou, C.-Y. Yang, L. Zou, X. Meng, W. Ma, J.-Y. Wang, J. Pei, *Adv. Mater.* **2017**, *29*, 1701072.

[24] a) A. Mazaheripour, S. Majumdar, D. Hanemann-Rawlings, E. M. Thomas, C. McGuinness, L. d'Alencon, M. L. Chabinyc, R. A. Segalman, *Chem. Mater.* **2018**, *30*, 4816; b) D. Zhao, A. Martinelli, A. Willfahrt, T. Fischer, D. Bernin, Z. U. Khan, M. Shahi, J. Brill, M. P. Jonsson, S. Fabiano, X. Crispin, *Nat. Commun.* **2019**, *10*, 1093; c) A. K. K. Kyaw, G. D. H. Wong, T. A. Yemata, J. Xu, *Org. Electron.* **2019**, *69*, 7.

[25] a) J. H. O. Peng Wei, Guifang Dong, Zhenan Bao, *J. Am. Chem. Soc.* **2010**, *132*, 8852; b) B. D. Naab, S. Guo, S. Olthof, E. G. Evans, P. Wei, G. L. Millhauser, A. Kahn, S. Barlow, S. R. Marder, Z. Bao, *J. Am. Chem. Soc.* **2013**, *135*, 15018; c) D. Kiefer, A. Giovannitti, H. Sun, T. Biskup, A. Hofmann, M. Koopmans, C. Cendra, S. Weber, L. J. Anton Koster, E. Olsson, J. Rivnay, S. Fabiano, I. McCulloch, C. Muller, *ACS Energy Lett.* **2018**, *3*, 278; d) L. Qiu, J. Liu, R. Alessandri, X. Qiu, M. Koopmans, Remco W. A. Havenith, S. J. Marrink, R. C. Chiechi, L. J. Anton Koster, J. C. Hummelen, *J. Mater. Chem. A* **2017**, *5*, 21234.

[26] a) M. Schwarze, C. Gaul, R. Scholz, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortman, K. Leo, *Nat. Mater.* **2019**, *18*, 242; b) S. Olthof, S. Mehraeen, S. K. Mohapatra, S. Barlow, V. Coropceanu, J. L. Bredas, S. R. Marder, A. Kahn, *Phys. Rev. Lett.* **2012**, *109*, 176601.

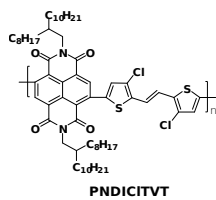
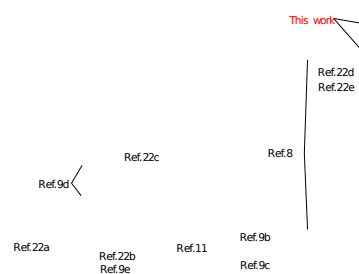
a**b**

Figure 1. (a) The chemical structures of polymers and dopants used in this paper. (b) Power factors of reported papers and this work. NDI-TBAF is not pure and used as mixing complex for n-type organic thermoelectrics.

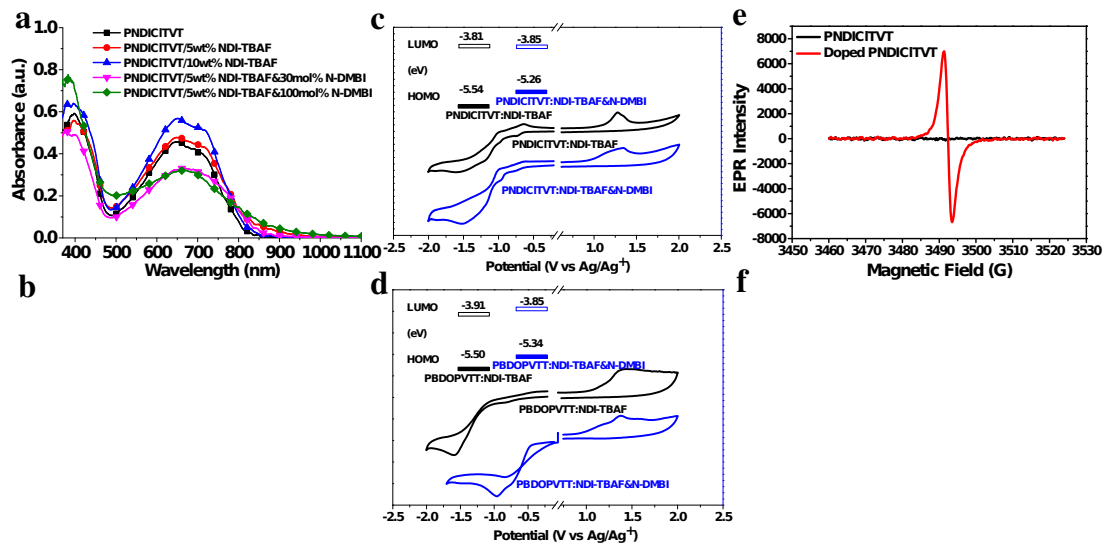


Figure 2. The UV-vis-NIR absorption spectra of (a) intrinsic and doped PNDICITVT and (b) intrinsic and doped PBDOPVTT polymer films. Cyclic voltammograms and energy levels of (c) doped PNDICITVT and (d) doped PBDOPVTT polymer films. EPR spectra of (e) intrinsic and doped PNDICITVT and (f) intrinsic and doped PBDOPVTT polymer films.

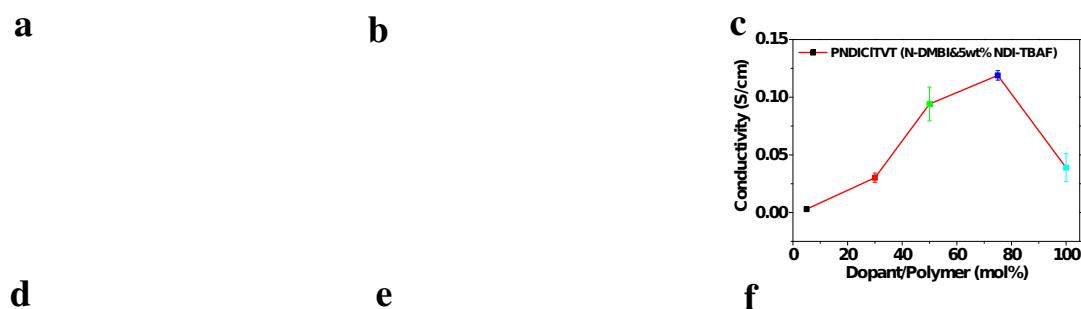


Figure 3. Electrical conductivity of PNDICITCT doped with (a) NDI-TBAF, (b) N-DMBI and (c) N-DMBI & 5 wt% NDI-TBAF. Seebeck coefficient and power factor of PNDICITCT doped with (d) NDI-TBAF, (e) N-DMBI and (f) N-DMBI & 5 wt% NDI-TBAF.

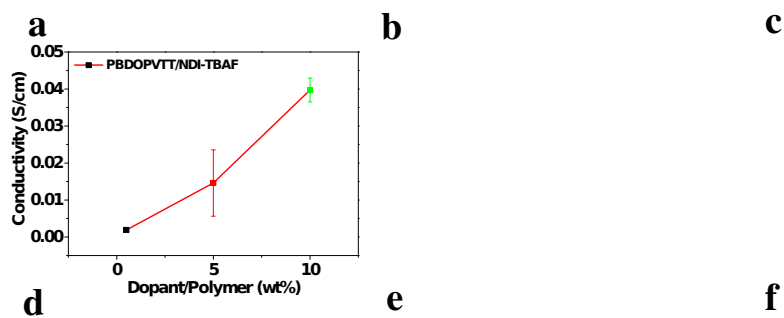


Figure 4. Electrical conductivity of PBDOPVTT doped with (a) NDI-TBAF, (b) N-DMBI and (c) N-DMBI & 5 wt% NDI-TBAF. Seebeck coefficient and power factor of PBDOPVTT doped with (d) NDI-TBAF, (e) N-DMBI and (f) N-DMBI & 5 wt% NDI-TBAF.

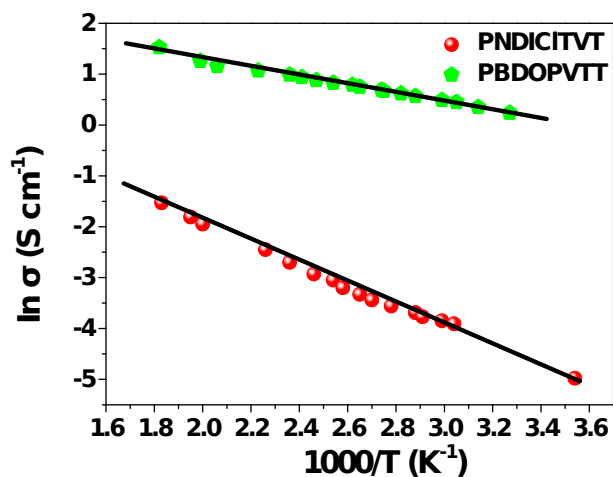


Figure 5. Temperature-dependent σ values of PNDICITVT and PBDOPVTT doped with co-dopants.

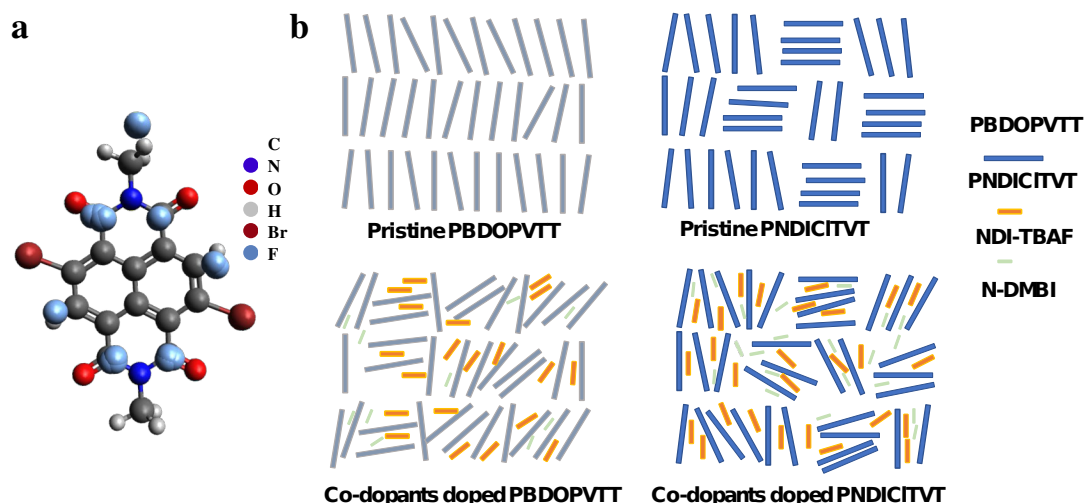


Figure 6. (a) Atomic-scale representation of the preferred locations for fluoride ion (pale blue) complexation above a representative motif of the N,N-dimethyl NDI backbone. (b) Schematic of molecular packing in pristine polymer films and doped polymer films.

Pre-formed Meisenheimer complexes of NDI-TBAF are obtained by mixing NTCDI and TBAF in solution and suitable for application in *n*-type organic thermoelectrics. NDI-TBAF doped PNDICITVT produces a PF of $67 \mu\text{W m}^{-1} \text{K}^{-2}$. Co-dopants of N-DMBI and NDI-TBAF-doped PNDICITVT and PBDOPVTT show high PF values of 35 and $58 \mu\text{W m}^{-1} \text{K}^{-2}$, respectively.

J. Han, C. Ganley, Q. Hu, X. Zhao, P. Clancy, T. P. Russell, H. E. Katz*

Using pre-formed Meisenheimer complexes as dopant for n-type organic thermoelectrics with high Seebeck coefficient and power factor

ToC figure

