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Understanding the Effects of Molecular Dopant on n-Type Organic Thermoelectric Properties

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Abstract

Molecular doping is a powerful method to fine-tune the thermoelectric properties of organic semiconductors, in particular to impart the requisite electrical conductivity. The incorporation of molecular dopants can, however, perturb the microstructure of semicrystalline organic semiconductors, which complicates developing a detailed understanding of structure-property relationships. To better understand how the doping pathway and the resulting dopant counterion influence the thermoelectric performance and transport properties, we developed a new dimer dopant, (N-DMBI)₂. Subsequently, we then n-doped FBDPPV with dimer dopants (N-DMBI)₂, (RuCp*mes)₂, and the hydride-donor dopant N-DMBI-H. By comparing the UV-*vis*-NIR absorption spectra and morphological characteristics of the doped polymers, we find that not only the doping mechanism, but also the shape of the counterion strongly influence the thermoelectric properties and transport characteristics. (N-DMBI)₂, which is a direct electron-donating dopant with a comparatively small, relatively planar counterion, gives the best power factor among the three systems studied here. Additionally, temperature-dependent conductivity and Seebeck coefficient measurements differ between the three dopants with (N-DMBI)₂ yielding the best thermoelectric properties. The results of this study of dopant effects on thermoelectric properties provide insight into guidelines for future organic thermoelectrics.

1. Introduction

Organic thermoelectric (OTE) materials have garnered increased attention because of their potential to enable flexible and wearable devices that can convert waste heat into electricity.^[1] The efficacy of a TE material in this energy conversion is given by the dimensionless figure of merit $ZT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. In comparison to traditional inorganic TE materials, OTEs typically have advantageously low thermal conductivities ($0.1 \leq 1 \text{ W m}^{-1} \text{ K}^{-1}$), but less favorable electronic properties; therefore, research is focused on optimizing the power factor (PF), $S^2\sigma$. The PF of organic semiconductors can be fine-tuned using a variety of synthetic techniques (doping, synthetic modification, processing, *etc.*),^[2] but often S and σ are anticorrelated, making PF optimization nontrivial. Decoupling S and σ so that both parameters can be improved simultaneously remains a challenge for the field.

A powerful method to fine-tune the thermoelectrical properties in organic semiconductors is molecular doping, where a dopant molecule creates additional charge carriers by reducing or oxidizing these organic semiconductors.^[3] Several studies have reported new conjugated organic backbones and their structure-property relationships,^[2c,2f-2j] and doping with a wide variety of molecular dopants.^[4] Unlike traditional inorganic semiconductors, where dopant atoms are covalently bonded to the surrounding matrix and are homogeneously incorporated on the atomic scale, doped organic semiconductors consist of spatially heterogeneous dopants that are coulombically bound to the organic matrix.^[5] The addition of molecular dopants impacts the organic matrix morphology, and the interrelationship between molecular dopant, aggregation, and material properties in OTEs is still not fully understood.

For impactful OTE device architectures to be realized, both p- and n-type OTE materials with high PF s are needed. Efficient p-type materials and high PF s have been

reported,^[2a-2c,6] but progress on n-type materials still lags far behind because of their relatively low charge-carrier mobility values and, often, the lower stability of n-doped materials in various environments.^[7] Although numerous n-type OTEs are being explored, including new conjugated polymers^[2g,2i] and metal-organic structures,^[8] additional investigations on n-type systems are essential for advancing OTEs.

The work described here investigates the effects of dopant selection on the morphological, thermoelectric properties of n-doped FBDPPV (see **Figure 1**) with dimeric dopant (RuCp*mes)₂ and hydride dopant N-DMBI-H (although this dopant has often been referred to as “N-DMBI”, we use “N-DMBI-H” here to emphasize that a hydrogen atom as well as an electron must be lost to form the N-DMBI⁺ cation; **Figure 1**). To decouple the effects of differing doping mechanism from the counterion size, we also developed a dimer n-dopant, (N-DMBI)₂, that behaves in a similar way to (RuCp*mes)₂ (*i.e.*, which forms the same N-DMBI⁺ cation as N-DMBI-H, but without involving a hydrogen atom or hydride transfer). Using spectroscopic, structural characterization, and thermoelectric property measurements as functions of dopant species and concentration we found that (N-DMBI)₂ dopes FBDPPV most efficiently and produces the optimum thermoelectric properties. Finally, we performed temperature-dependent thermoelectric measurements to elucidate the charge-transport mechanisms. We conclude that charge transport in doped FBDPPV is best described by thermally activated polaron hopping (Mott polaron model), and that the electronic structure is dependent on the dopant. This study shows the importance of dopant selection for optimized n-type OTE materials and provides insight into design guidelines for future n-type OTEs.

2. Results and Discussion

2.1 Design and Synthesis of (N-DMBI)₂

2-Substituted-1,3-dimethylbenzimidazole derivatives of several types – hydride derivatives, Y-DMBI-H, such as N-DMBI-H (**Figure 1**); halide salts of benzoimidazolium cations, Y-DMBI^+ , that release the corresponding radicals on sublimation; and dimers, $(\text{Y-DMBI})_2$, formed by such radicals – and dimeric organometallic compounds, such as $(\text{RuCp}^*\text{mes})_2$, are some of the most efficient n-dopants (so far) in terms of achieving the highest electrical conductivities with both the small molecule C_{60} and the polymer P(NDI2OD-T2) (**Figure 2, S1**, and see **Figure 1** for a summary of n-dopant molecules used). Use of Y-DMBI-H molecules, such as N-DMBI-H, inevitably involves hydride and/or hydrogen-transfer reactions,^[9] and the fate of the hydrogen atom in the n-doped systems is in many cases unknown; in contrast, $(\text{Y-DMBI})_2$ and $(\text{RuCp}^*\text{mes})_2$ dimers are known to react effectively and cleanly with electron acceptors to contribute two electrons and form two monomeric cations, Y-DMBI^+ or $\text{RuCp}^*\text{mes}^+$, respectively.^[10] In addition to differing mechanisms, different cation geometries are available through Y-DMBI-H and dimer approaches, which can be important since counterions can impact aggregation and morphology in solid-state, and hence thermoelectric properties. The differences in the shapes of the cations used in this work are evident in both DFT-optimized gas-phase geometries (**Figure 2c**) and in the single-crystal X-ray structures of $\text{RuCp}^*\text{mes}^+\text{I}^-$ and $\text{N-DMBI}^+\text{PF}_6^-$ (**Figure S3** and **S4**). The dopant cation sizes are fairly similar (molecular volumes based on the X-ray geometries are 2388 and 2176 bohr³, respectively); however, the organometallic cation is a bulky cylindrical shape, similar to that of other sandwich compounds,^[4d] whereas N-DMBI^+ has a more planar structure but with a significant twist between the planes formed by the imidazolium and arene portions of the cation (51.9° in the optimized structure (**Figure 2c**); 52.6° in the crystal structure of its PF_6^- salt (**Figure S4**)). Although, as noted above, Y-DMBI dimers are known, those reported to date have all employed bulkier 2-substituents (Y = cyclohexyl, ferrocenyl, ruthenocenyl) rather than planar aryl groups.^[4f,10b] Given that high conductivity values have been obtained in some systems using N-DMBI-H, and in others

using (RuCp*mes)₂, we reasoned that the hypothetical dimer (N-DMBI)₂ would help us to decouple the role of cation shape from the reaction pathway, and to understand how these variables affect thermoelectric properties.

We found that the new dimer (N-DMBI)₂ (**Figure 1**) could be synthesized through Na-Hg reduction of N-DMBI⁺PF₆⁻ in 85% yield. NMR characterization does not unambiguously confirm the structure of the reduction product, with the ¹H spectrum exhibiting broad features and the ¹³C spectrum numerous resonances, likely due to restricted rotation. However, elemental analysis, mass spectrometry (showing, as is typical for dimeric reductants, the corresponding monomer cation), electrochemical data (**Figure S5**), and chemical reactivity as a reductant are consistent with the proposed dimeric structure. The effective redox potential of the dimer, $E(D^+/0.5D_2)$, is estimated to be ca. -2 V vs. FeCp₂⁺⁰ (see details in Supporting Information, **Figure S5**), similar to that of other (Y-DMBI)₂ species^[10b] and of (RuCp*mes)₂^[4d], but is certainly at least as reducing as -1.45 V, as evidenced by its reduction of TIPS-pentacene to the corresponding radical anion (**Figure S6**).

In the following sections, we compare N-DMBI-H, (RuCp*mes)₂ (synthesized in 88% yield by a modification of literature procedures that, as described in the supporting information, replaces hazardous liquid alkali metals by silica-gel-supported sodium-potassium alloy), and (N-DMBI)₂ as n-dopants for polymer FBDPPV in terms of their effects on spectra, thermoelectric properties, structure, and morphology.

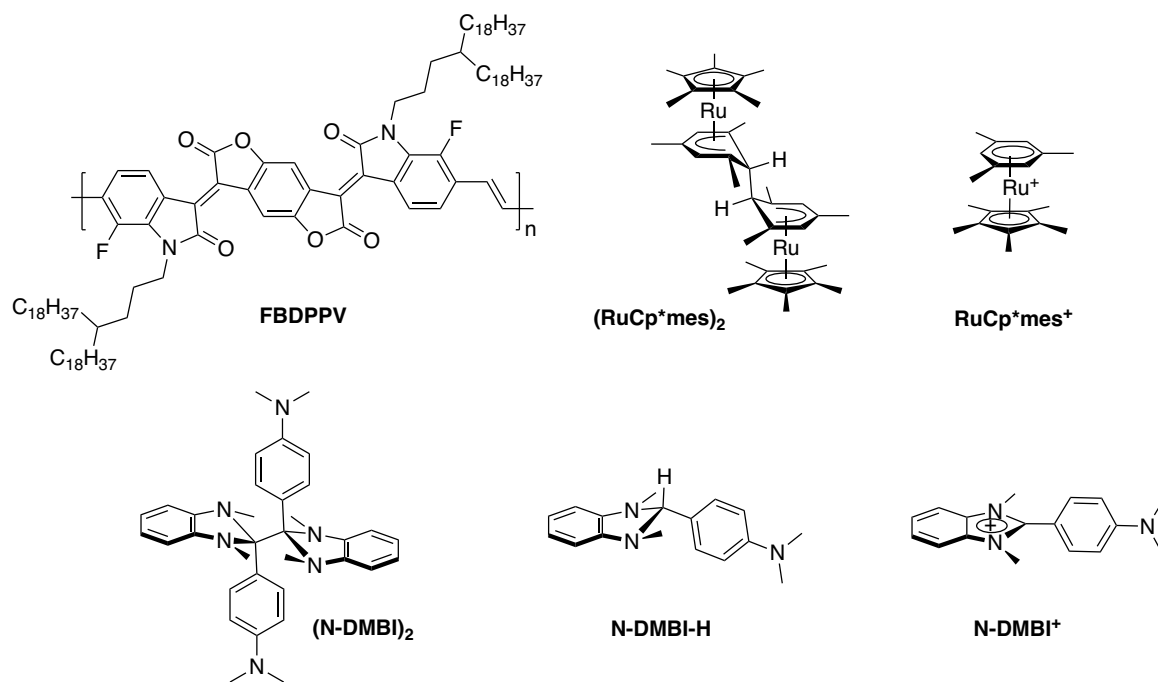


Figure 1. Chemical structures of polymer FBDPPV and dopants (RuCp*mes)₂, (N-DMBI)₂, and N-DMBI-H, along with those of the corresponding cations.

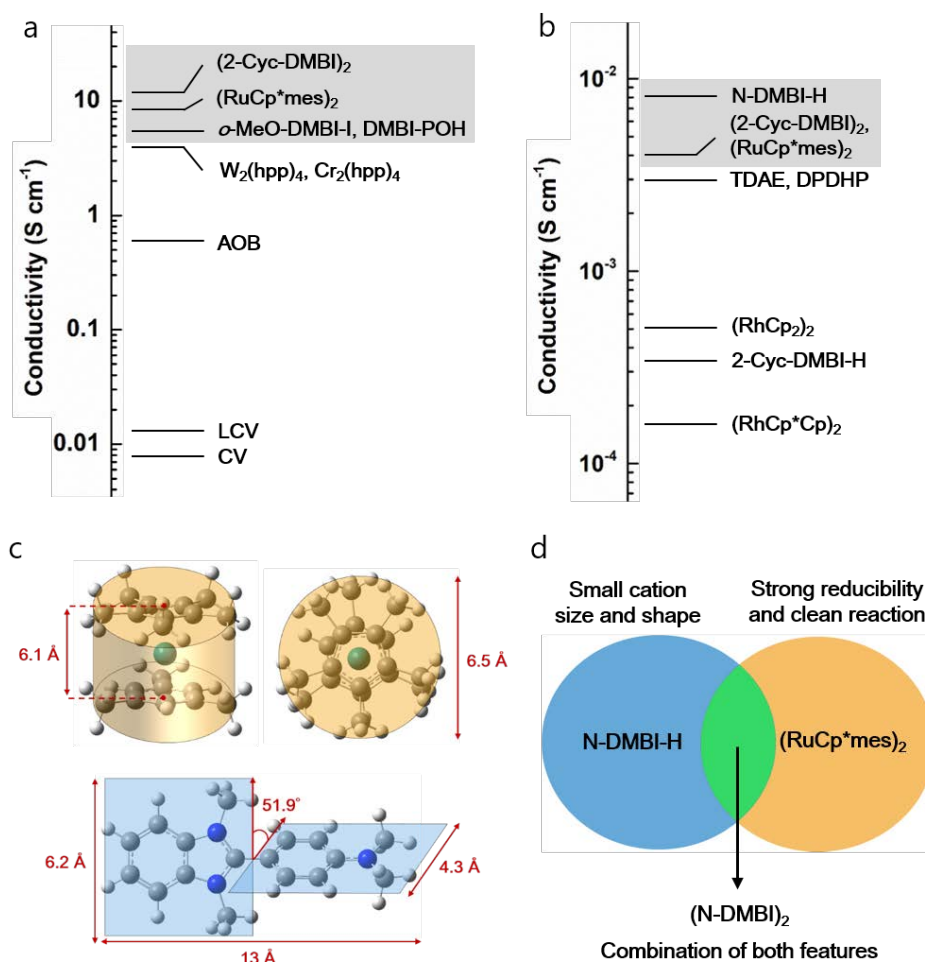


Figure 2. Summary of electrical conductivities of n-doped small molecule C₆₀ (a) and polymer P(NDI2OD-T2) (b) with various dopants (see Figure S1 and S2 for chemical structures of the semiconductors and the dopants). (c) Optimized molecular structures of dopant cations. Top: RuCp*mes⁺ (m062x/genecp LANL2DZ); bottom: N-DMBI⁺ (uw97xd/6-311++g(d,p)) (see Figure 1 for chemical structures). (d) Design concept for (N-DMBI)₂.

2.2 UV-vis-NIR and Thermoelectric Measurements

The doping behavior of the three dopants was investigated using UV-vis-NIR spectroscopy of doped FBDPPV films. **Figure 3** shows that pristine FBDPPV has absorption peaks at 490, 710, and 785 nm. Upon doping, an absorbance peak at 1000 nm and a broad mid-infrared (MIR) absorption emerge in all systems with a concomitant decrease in the absorption peaks of the undoped polymer. The increased MIR absorption intensity with increasing doping concentration is consistent with a greater extent of reduction by the dopants. In comparing doping effects, it is important to note that the dimeric molecules, (RuCp*mes)₂ and (N-DMBI)₂, are expected to each contribute two electrons and form two monomeric cations,^[4c,4d,4f,10] while N-DMBI-H can only contribute a single electron per molecule.^[9]

Polymers doped with 25 mol% dimer (*i.e.* potentially corresponding to two electrons for every three polymer repeat units) show a lower absorbance ratio of neutral polymer (*i.e.*, around 710 and 785 nm) to polaron (*i.e.*, over 1000 nm) than polymer doped with 50 mol% N-DMBI-H (potentially a higher doping level of one electron per repeat unit), qualitatively indicating that the dimer dopants have a higher doping efficacy.

The spectral changes with increased doping levels are qualitatively similar for both types of dopants: a feature peaked at ca. 1000 nm (with a subsidiary peak discernable in some cases at ca. 1300 nm), attributed to polaronic absorption, was observed, along with a broad feature extending into the MIR. At the highest levels of reduction (*i.e.*, 50 mol% loadings of the dimeric dopants (RuCp*mes)₂ and (N-DMBI)₂, corresponding to two electrons per repeat unit), a distinct broad peak is seen around 1700 nm. This may be associated with a

compressed polaron, bipolaron, or π -dimer species with similar energetics to the original polaron absorption at 1100 nm.^[11]

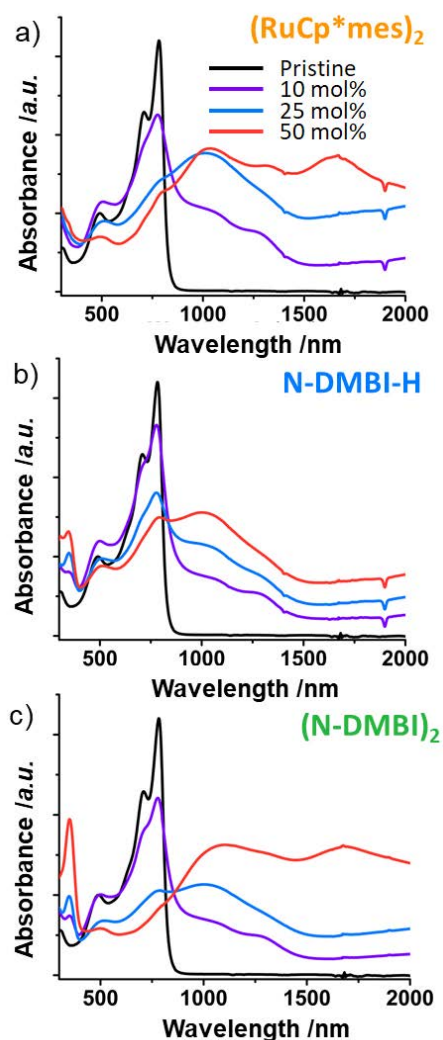


Figure 3. UV-*vis*-NIR absorption spectra of doped FBDPPV films as a function of dopant and doping ratio. a), b), and c) doped with (RuCp*mes)₂, N-DMBI-H, and (N-DMBI)₂, respectively.

To understand how the dopant-induced electronic states impact thermoelectric properties, the electrical conductivity and the Seebeck coefficient were measured on doped films. As shown in **Figure 4a**, the highest electrical conductivity for FBDPPV doped with (RuCp*mes)₂ is 1.6 S cm⁻¹ at 23 mol% dimer. However, FBDPPV reaches an even higher

electrical conductivity of ca. 8 S cm^{-1} with N-DMBI-based dopants. The maximum electrical conductivity observed is with 10.7 mol% (N-DMBI)₂ or 43 mol% N-DMBI-H, the data for the latter agreeing well with our previous reports.^[2g] To reach highest electrical conductivity, the amount of N-DMBI-H is considerably more than double that of (N-DMBI)₂, suggesting that the dimer (N-DMBI)₂ dopes more efficiently than N-DMBI-H (even when its ability to contribute two rather than one electrons is taken into account), consistent with the optical data discussed above (**Figure 3**). The higher electrical conductivities in N-DMBI⁺ systems relative to those in the RuCp*mes⁺ system further affirms the importance of dopant selection for conductivity optimization, and, therefore, perhaps thermoelectric property optimization as discussed below.

As dopant species are introduced into the FBDPPV films, the Seebeck coefficient (*S*) changes. The Seebeck coefficient is less sensitive to morphology and more dependent on transport parameters and energy levels.^[2a,12] **Figure 4b** shows that the Seebeck coefficients of all films are negative (n-type behavior), as expected; values are -113, -63, and -150 $\mu\text{V K}^{-1}$ at ca. 12 mol% for the dimers (RuCp*mes)₂ and (N-DMBI)₂, and at ca. 24 mol% for N-DMBI-H, respectively. For the dimer dopants, this roughly equates to one electron donated for every 3.7 repeat units. For N-DMBI-H, this roughly equates to one electron potentially donated for every 3.2 repeat units. A smaller (magnitude) Seebeck coefficient is indicative of a higher extent of doping; therefore, based on Seebeck coefficient measurements and the nearly comparable dopant electron to monomer ratio, (N-DMBI)₂ is the most efficient dopant in this study.

The dopant concentrations corresponding to optimal thermoelectric *PF* depend on the interplay of the trends in conductivity and in the Seebeck coefficient. Dopants initially increase the electrical conductivity by introducing mobile charge carriers, but at higher dopant concentrations the electrical conductivity subsequently decreases by deleteriously impacting

morphology and increasing carrier scattering; whereas, as noted above, the magnitude of the Seebeck coefficient decreases. **Figure 4c** shows the PF for the FBDPPV systems; the best PF we obtained for a FBDPPV film is ca. $7 \mu\text{W m}^{-1} \text{K}^{-2}$ for the case of doping with 9.2 mol% (N-DMBI) $_2$.

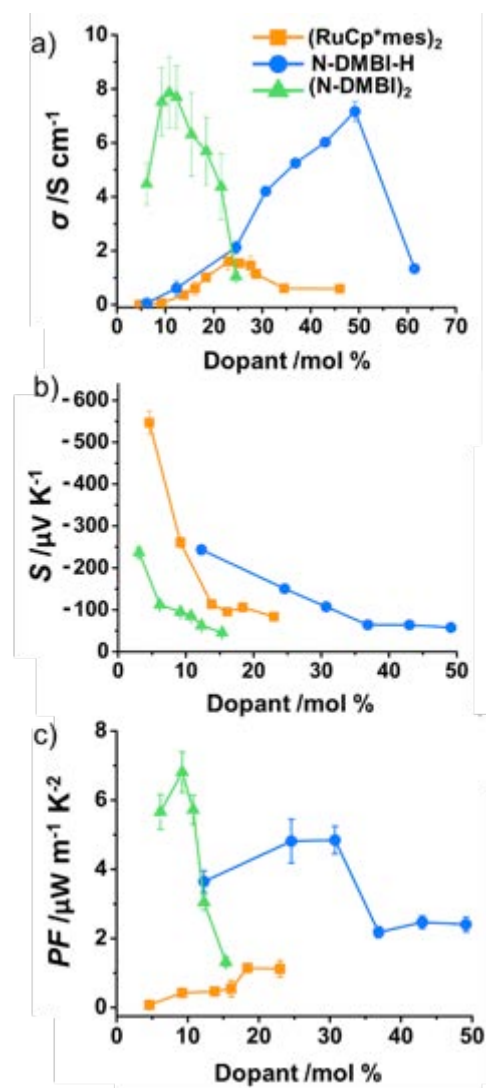


Figure 4. Electrical and thermoelectric properties of (RuCp*mes) $_2$ -, N-DMBI-H-, and (N-DMBI) $_2$ -doped FBDPPV at varying dopant concentrations. a) Electrical conductivity, b) Seebeck coefficient, and c) power factor. Error bars represent sample to sample error, measurement error, and the error propagation, respectively. Some error bars are obscured by the data point.

2.3 Microstructural Characterization

To further develop an understanding of dopant geometry-polymer morphology-thermoelectric property relationships, grazing-incidence wide-angle X-ray scattering (GIWAXS), atomic force microscopy (AFM), and scanning Kelvin probe microscopy (SKPM) measurements were performed. The neat film of FBDPPV is crystalline and smooth (**Figure 5a,e**), and the out-of-plane multiple order scattering features (along the q_z axis) of the lamellar packing ($h00$) and the signal for both face-on (along the q_z axis) and edge-on (along the q_{xy} axis) π - π stacking (010) are clearly observed (**Figure 5a**). For the doping concentrations that yielded the highest electrical conductivity for each dopant-polymer system, the lamellar distance increases from 29.6 Å (neat film) to over 31 Å in all cases (**Table 1**). Notably, only (100) can be observed in the RuCp*mes⁺ system while the two N-DMBI⁺ systems still exhibit multiple order scattering features (**Figure 5b-d**). Additionally, the π - π stacking distance shows negligible change in the two N-DMBI⁺ systems, but ordered π - π stacking is lost in the RuCp*mes⁺ system (**Figure 5b-d, Table 1**). In over-doped systems, the lamellar distance in the RuCp*mes⁺ system increases by 12% (for 46 mol% doping), whereas the lamellar spacing of N-DMBI-H (86 mol%) and (N-DMBI)₂ (43 mol%) systems are largely maintained and the π - π distances increases (**Table 1, Figure S7a-c**). These results may indicate that for the N-DMBI-H and (N-DMBI)₂ systems there is excess space for facile intercalation of the relatively small and more planar N-DMBI⁺ in the lamellar alkyl side-chain region, so that it less significantly impacts the π - π stacking, while bulky RuCp*mes⁺ resides not only enlarges the lamellar distance but also strongly disrupts the π - π interaction.

AFM and SKPM were used to further characterize the relationships between dopant, film topography, and the measured thermoelectric properties. AFM surface morphology characterization reveals that the highest conductivity films maintained the pristine fibril

microstructure, independent of dopant (**Figure 5e-h**). Moreover, all surface roughness measurements in the optimally doped films were lower than 1 nm (**Table 1**). SKPM was used to probe for structural homogeneity based on spatial fluctuations in the work function (potential).^[13] Homogenous surface potential mappings (**Figure 5j-l**) and narrow potential contrast distribution (**Figure S8b**) showed good miscibility (no obvious phase separation) in all optimally-doped films. The morphology and chemical homogeneity of optimally doped FBDPPV films are minimally impacted by the dopant species, also showing good miscibility, but (as discussed above) GIWAXS data indicates that the molecular packing is significantly dependent on the type of dopant cation.

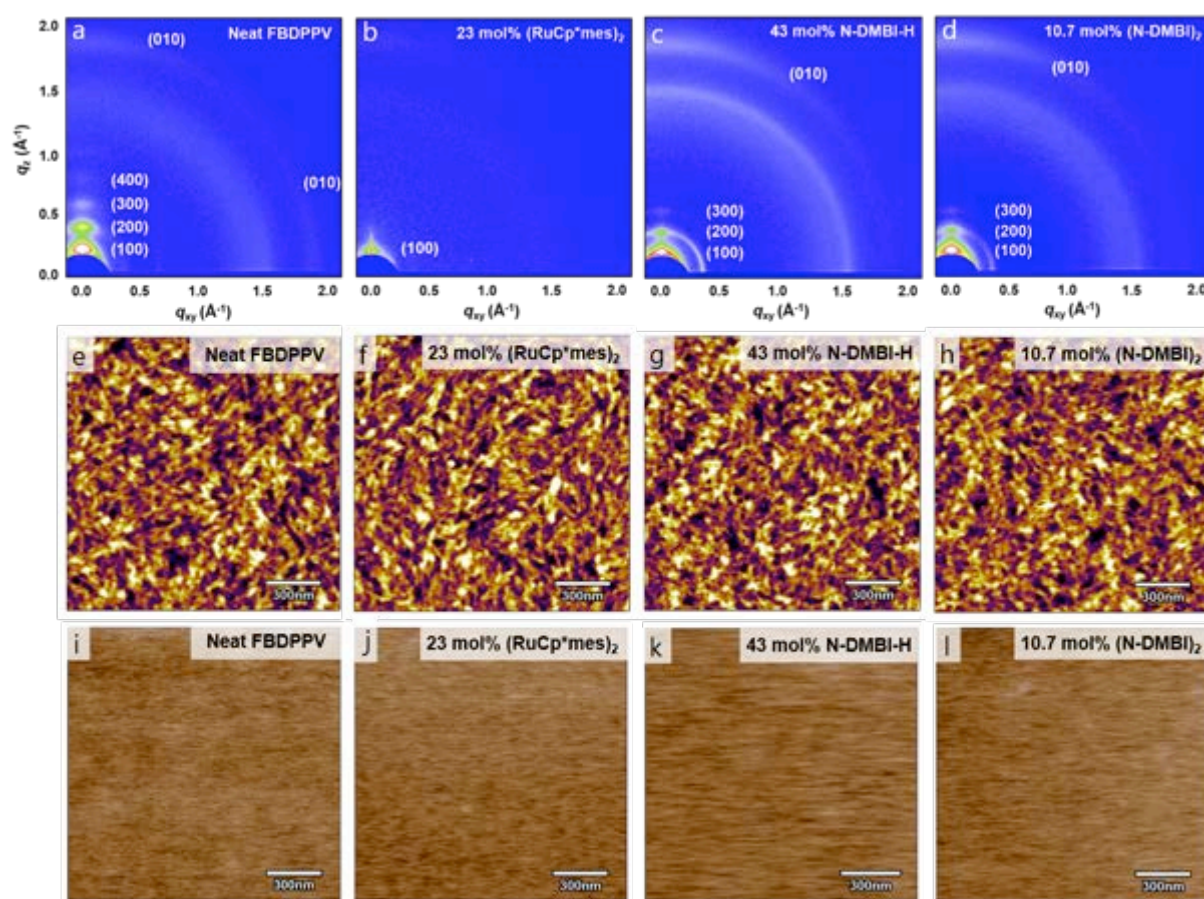


Figure 5. Microstructure and morphology study of **neat FBDPPV**, and (RuCp*mes)₂-, N-DMBI-H-, and (N-DMBI)₂-doped FBDPPV as functions of dopant and doping concentration. (a)-(d) GIWAXS images; (e)-(h) surface topograph mapping by AFM; (i)-(l) potential mapping by SKPM. The dopant and doping molar concentration is shown in inset.

Table 1: Summary of molecular arrangements and surface roughness collected by GIWAXS and AFM for FBDPPV-(RuCp*mes)₂, FBDPPV-(N-DMBI), and FBDPPV-(N-DMBI)₂ systems.

System	Lamellar distance [Å]	π - π distance [Å]	Roughness [nm] ^{a)}
Neat FBDPPV	29.6	3.38	0.9
23 mol% (RuCp*mes) ₂	31.3	N/A	0.7
46 mol% (RuCp*mes) ₂	33.1	N/A	5.7
43 mol% N-DMBI-H	31.1	3.41	0.8
86 mol% N-DMBI-H	31.7	3.45	1.2
10.7 mol% (N-DMBI) ₂	31.1	3.39	0.7
43 mol% (N-DMBI) ₂	31.6	3.49	2.7

^{a)} Roughness was measured by AFM.

2.4 Temperature-Dependent Thermoelectric Properties, and Transport Models

Since OTE materials are not perfectly crystalline, charge transport can be analyzed by using transport formalisms developed for disordered materials.^[14] Additional transport parameters can be extracted through non-linear regression of both the temperature-dependent electrical conductivity and Seebeck coefficient measurements.^[2c,8a,15] In this study, we performed temperature-dependent electrical conductivity and Seebeck coefficient measurements on each dopant system at the doping concentrations with the highest electrical conductivity (*i.e.*, 23 mol% for (RuCp*mes)₂, 43 mol% for N-DMBI-H, and 10.7 mol% for (N-DMBI)₂). We observed that as temperature increases, electrical conductivity increases in all systems (**Figure 6a**), but in contrast, the Seebeck coefficients show a less evident temperature-dependence (**Figure 6b**). Based on the aforementioned observations, (specifically, the UV-vis-NIR polaronic signatures (**Figure 3**), the charge transport dependence on the extent of doping (**Figure 4**), and the temperature-activated electrical conductivity (**Figure 6**)), we explored the possibility that these materials exhibit characteristics that are phenomenologically consistent with the Mott polaron model.

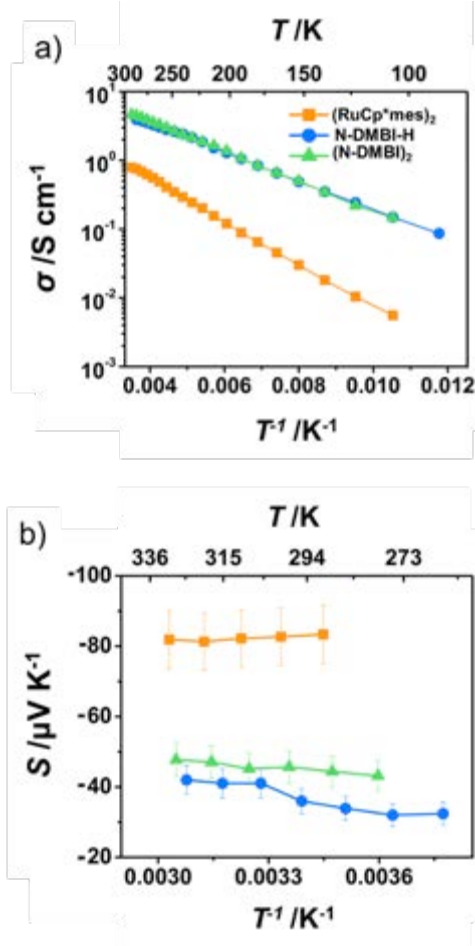


Figure 6. (a) Electrical conductivity and (b) Seebeck coefficients as a function of temperature. Doping concentrations are 23 mol% for (RuCp*mes)₂, 43 mol% for N-DMBI-H, and 10.7 mol% for (N-DMBI)₂.

The Mott Polaron model expresses electrical conductivity, σ , and Seebeck coefficient, S , as functions of material charge transport constants that can be isolated with temperature dependent measurements (**Equation 1,2**). Here,

$$\sigma = \sigma_0 \exp\left(\frac{-(E+W_H)}{k_b T}\right), \quad (1)$$

$$S = \left(\frac{k_b}{e}\right) \left(\frac{E}{k_b T} + S_0\right), \quad (2)$$

where e is the electron charge. σ_0 is the pre-exponential conductivity that heavily depends on film morphology and hopping distance, and represents a maximum electrical conductivity achievable. E is the (average) ionization energy of the donor states and W_H is the energetic spread of states. Collectively, E and W_H (*i.e.*, $E + W_H$) represent an Arrhenius activation energy (E_a) that is related to the energy barrier for charge transport.^[17] In **Equation 2**, S_0 is a constant.^[15b] In a similar study, Emin, Crispin, and coworkers attributed S_0 to be a nearly temperature-independent constant associated with the bipolaron carrier concentration in doped poly(thiophene).^[15a,15c] The carrier concentration contribution to the Seebeck coefficient is often expressed as an entropy of mixing term whose functional form is $S_0 = \ln\left(\frac{1-c}{c}\right)$, where c is the ratio of transport-active polarons to thermally accessible hopping sites, but the functional form (admittedly) can vary depending on the polaronic species interactions. Based on these previous studies, we express the Seebeck coefficient as:

$$S = \left(\frac{k_b}{e}\right) \left(\frac{E}{k_b T} + \ln\left(\frac{1-c}{c}\right)\right) \quad (3)$$

Using this Mott polaron model (**Equation 1-3**), and the data in **Figure 6**, the aforementioned transport constants for these FBDPPV systems were extracted via non-linear regression. Looking at $\ln(\sigma)$ vs. $1/T$, the y-intercepts are indicative of $\ln(\sigma_0)$, and the slopes are indicative of $\frac{-E_a}{k_b}$. Similarly, looking at S vs. $1/T$, the y-intercepts are indicative of $\left(\frac{k_b}{e}\right) \cdot S_0$, and the slopes are indicative of $\left(\frac{E}{e}\right)$. Values for σ_0 , E_a , and S_0 were evaluated for statistical significance using a t-tests and a 95% confidence interval. It was found that σ_0 , E_a , and S_0 can be significantly extracted from the collected data with P-values orders of magnitude lower than the significance level (0.05); P-value for σ_0 on the order of 10^{-29} to 10^{-20} , for E_a on the order of 10^{-29} to 10^{-25} , for S_0 on the order of 10^{-5} to 10^{-4} . Therefore, we can reject the null hypothesis that these transport constants cannot be significantly extracted from the (arguably sparse) data set. **Figure 7** shows σ_0 , E_a , S_0 constants with their associated 95%

confidence interval represented by the error bars. RuCp*mes⁺ has a higher E_a (62.4 meV) compared to that with either N-DMBI-H (41.7 meV) or (N-DMBI)₂ (43.4 meV). Additionally, the RuCp*mes⁺ system shows the lowest σ_0 (10.1 S cm⁻¹) compared to that with either N-DMBI-H (23.8 S cm⁻¹) or (N-DMBI)₂ (27.9 S cm⁻¹). The lower σ_0 and higher E_a for the FBDPPV-(RuCp*mes)₂ system relative to what is seen for the N-DMBI⁺-containing systems may well arise from the greater disruption of the microstructure observed in the GIWAXS data as illustrated by the π - π distance shown in **Table 1**.

Extracted S_0 constants were further evaluated to better understand fractional carrier occupancies (c). As the amount of doping increases, c should increase, S_0 should decrease, and the magnitude of the Seebeck coefficient should decrease (**Equation 2,3**); this inverse relationship between c and $|S|$ is well aligned with the observed doping-Seebeck coefficient trends shown in **Figure 4** and is commonly found in organic thermoelectric literature. **Figure 7c** shows S_0 values, which should similarly show an inverse relationship with c , and is less commonly evaluated in the organic thermoelectric literature. S_0 increases from (N-DMBI)₂ to (RuCp*mes)₂ to N-DMBI-H (0.72 to 0.93 to 1.32, respectively), implying c should decrease from (N-DMBI)₂ to (RuCp*mes)₂ to N-DMBI-H; however the doping ratio is 10.7, 23, and 43 mol% for (N-DMBI)₂, (RuCp*mes)₂, and N-DMBI-H respectively. Although we do not know exactly how many carriers each dopant creates, these relationships lead us to believe that (N-DMBI)₂ is the most effective dopant to create transport-active polaronic species (carriers) per accessible hopping sites in FBDPPV. Additionally, the anticipated direct relationship between calculated S_0 and measured $|S|$ was not observed. S_0 decreases from N-DMBI-H (1.32) to (RuCp*mes)₂ (0.93) to (N-DMBI)₂ (0.72), but $|S|$ decreases from (N-DMBI)₂ $\approx$ (RuCp*mes)₂ (85 μ V K⁻¹) to N-DMBI-H (58 μ V K⁻¹). One reason for this observed difference could be that the polaronic species created in each dopant system could have different inter-polaronic interactions^[16] and therefore different ratios of transport-active polarons to thermally accessible hopping sites. This idea is further explored in **Figure S9**, comparing different

polaronic interaction models. Another reason could be that different doping counterions could have different impacts on energy-(in)dependent scattering processes (as seen in the Kang-Snyder empirical model, **Figure S10**).^[17] Although some uncertainties exist about the observed qualitative trends between S_0 and S , we observe that (N-DMBI)₂ is the best choice for the high PF in this study, and that additional temperature-dependent thermoelectric property measurements are needed (broadly) for the organic thermoelectrics community to better understand the underlying transport characteristics.

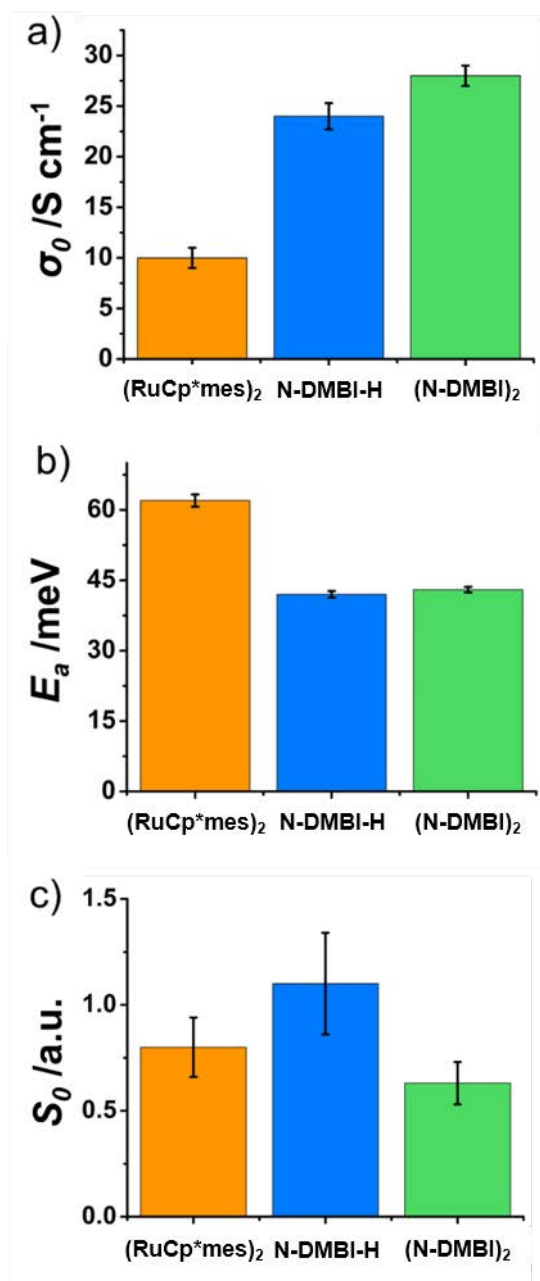


Figure 7. (a) Pre-exponential electrical conductivity (σ_0), (b) electrical conductivity activation energy (E_a), (c) and Seebeck coefficient constant (S_0) extracted from the temperature-dependent electrical conductivity and Seebeck coefficient measurements. Error bars represent a 95% confidence intervals in the non-linear regression.

3. Conclusion

In this work, we have developed a new dimeric n-dopant (N-DMBI)₂ and demonstrated the significance of doping selection on thermoelectric performance and transport characteristics of the conjugated polymer for OTEs. Dimer dopants (RuCp*mes)₂ and (N-DMBI)₂ create a unique polaronic species due to their much stronger reducing ability in comparison to the hydride dopant N-DMBI-H. The higher doping efficiency of (N-DMBI)₂ relative to N-DMBI-H, combined with the less pronounced effects of the smaller and more planar N-DMBI⁺ on the polymer relative to those of the bulky RuCp*mes⁺ cation yield a more ordered microstructure with longer delocalization length, and hence better thermoelectric performance. Additionally, temperature-dependent electrical conductivity and Seebeck coefficient measurements were used to elucidate that (N-DMBI)₂ has the lowest activation energy for charge transport in this study. These results suggest that, at least for the doping of ordered polymers, molecular dopants should be designed to have (i) more planar shape for less perturbation of ordered microstructures and (ii) clean and efficient electron-transfer reaction pathways.

Supporting Information

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

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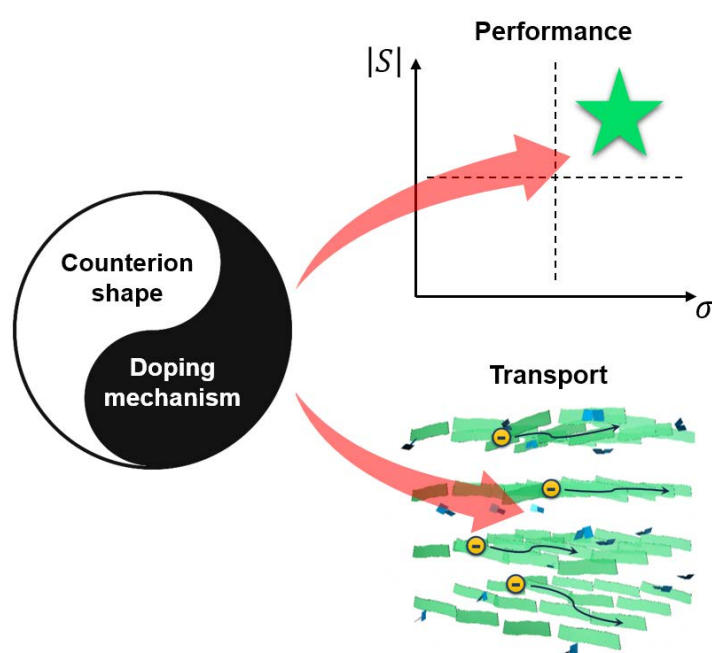
A novel dimeric n-dopant (N-DMBI)₂, is designed and synthesized to scientifically understand the effects of molecular dopant on thermoelectric properties. This study shows how the counterion shape, and the doping mechanism affect the thermoelectric performance and the transport pathway of n-type conducting polymers, and reveals what type of n-dopant is preferable.

Keyword: organic thermoelectrics, conducting polymers, doping, microstructure, dopants

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Understanding the Effects of Molecular Dopant on n-Type Organic Thermoelectric Properties

ToC figure



Supporting Information

Understanding the Effects of Molecular Dopant on n-Type Organic Thermoelectric Properties

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1. Materials: Synthetic Procedures and Characterizations

General: All commercially available chemicals were used without further purification unless otherwise noted. N-DMBI-H were purchased from Sigma-Aldrich. FBDPPV were synthesized following the previously reported procedures.^[S1] All operations involved in dimer synthesis were performed under an atmosphere of nitrogen using standard Schlenk techniques or in a glove box. Toluene and THF were dried using a solvent purification system from MBraun, benzene and hexane were dried using sodium, and NEt₃ was stored over KOH, and distilled prior to use. Sodium amalgam (1 wt%) was prepared immediately prior to use by addition of small pieces of Na metal to vigorously stirred Hg (electronic grade, 99.99%). ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AVIIIHD 500 MHz spectrometer and were referenced to tetramethylsilane using the residual proton signal of the solvent and the carbon resonances of the deuterated solvent, respectively. Mass spectra were measured on an Applied Biosystems 4700 Proteomics Analyzer using ESI mode. Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer. Electrochemical data were acquired using cyclic voltammetry in 0.1 M ⁿBu₄NPF₆ in dry THF under nitrogen, using a CH Instruments 620D potentiostat, a glassy carbon working electrode, a platinum wire auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride solution. A scan rate of 50 mV s⁻¹ was used and ferrocene was used as an internal reference.

(*RuCp*mes*)₂: This compound was synthesized by a modification of previous procedures, which used hazardous liquid alkali-metal reductants, either Na-Hg (which, in our hands, gives a lower yield than the literature)^[S2] or Na-K (which gives a high yield,^[S3] but is highly pyrophoric). Herein we used a stage 1 silica-gel supported Na-K alloy, NaK₂-SG(I), a commercially available solid that is stable to dry air.^[S4] Specifically, a slurry of [RuCp*mes]⁺PF₆⁻^[S5] (2.00 g, 3.98 mmol) in anhydrous THF was added to NaK₂-SG(I) (from Sigma-Aldrich, 4.96 g, 5 eq) under inert atmosphere. The reaction was stirred for 1 h at room

temperature. The solution was then decanted from the reductant via cannula and evaporated under reduced pressure. The solid residue was dissolved in toluene and the resulting solution was filtered through Celite, evaporated under reduced pressure, and dried under vacuum to yield pure (RuCp*mes)₂ as a pale yellow solid (1.26 g, 88%), ¹H and ¹³C{¹H} NMR spectra of which were consistent with previous reports.^[S2,S6]

[RuCp*mes]⁺I⁻: [RuCp*mes]⁺PF₆⁻^[S5] (0.40 g, 0.78 mmol), ⁿBu₄N⁺I⁻ (0.29 g, 0.78 mmol), and dry THF (6 mL) were charged to a vial under nitrogen; the resulting suspension was heated to 60 °C for 15 h. The reaction mixture was then allowed to cool to room temperature and diluted with diethyl ether (1.5 mL) to cause more solid product to precipitate. The resultant solid was filtered and washed with diethyl ether to obtain an off-white solid (0.32 g, 82%), shown by ¹H and ¹⁹F NMR to contain the [RuCp*mes]⁺ cation and negligible quantities of PF₆⁻, respectively, consistent with formation of the iodide salt. ¹H NMR (acetone-*d*₆, 400 MHz): δ 5.83 (s, 3H), 2.24 (s, 9H), 1.95 (s, 15H).

[N-DMBI]⁺PF₆⁻: A mixture of *N,N'*-dimethyl-*o*-phenylenediamine^[S7] (350 mg, 2.57 mmol) and 4-(dimethylamino)benzoylchloride (465 mg, 2.53 mmol) was heated to reflux in toluene (20 mL) under nitrogen for 1 h with vigorous stirring. After allowing to cool, the solids were collected by filtration, washed with copious hexane, and dried under vacuum. The solids were dissolved in water and the mixture was filtered to remove insoluble residues. An aqueous solution of NH₄⁺PF₆⁻ (5 mmol) was added to the filtrate with vigorous stirring. The light pink solid was collected by filtration, washed with water and then dried under vacuum. It was then recrystallized three times from CH₂Cl₂/Et₂O, and dried under high vacuum (424 mg, 40%). ¹H NMR (500 MHz, acetone-*d*₆): δ 8.01 (dd, *J*_{HH} = 6, 3 Hz, 2H), 7.75-7.72 (m, 4H), 7.05 (d, *J*_{HH} = 10 Hz, 2H), 4.08 (s, 6H), 3.15 (s, 6H). ¹³C{¹H} NMR (125 MHz, acetone-*d*₆): δ 154.1, 153.2, 133.2, 132.8, 127.4, 113.7, 112.6, 106.6, 40.0, 33.4. HRMS(ESI): Calculated for C₁₇H₂₀N₃ (M⁺ – PF₆): 266.1652; found: 266.1651. Anal. Calcd. for C₁₇H₂₀N₃PF₆: C 49.64, H 4.90, N 10.22. Found: C 49.87, H 4.94, N 10.09.

(*N*-DMBI)₂: A slurry of [N-DMBI]⁺PF₆⁻ (1.00 g, 2.43 mmol) were stirred in THF with 1 wt% Na-Hg (made from 280 mg Na and 28 g Hg) for 2 h at room temperature under nitrogen, during which time the color of the solution changed from light pink to colorless. The mixture was then decanted from the amalgam via cannula and evaporated under reduced pressure. The crude product was again extracted in toluene, filtered through Celite, and evaporated under reduced pressure to obtain a light yellow solid, which was further purified by passing through a short silica-gel column, which had been pre-treated with NEt₃, inside a nitrogen-filled glove box, with benzene as eluent. The benzene solution was evaporated, and the resulting solid was washed with hexane, and dried under vacuum to obtain pure (N-DMBI)₂ as light yellow solids (550 mg, 85%). ¹H NMR (500 MHz, benzene-*d*₆): δ 7.43-7.42 (br, 2H), 6.92-6.78 (br, 2H), 6.40-6.00 (br, 4H), 2.66-2.36 (br, 12H). HRMS(ESI): Calculated for C₁₇H₂₀N₃ ([M/2]⁺): 266.1652; found: 266.1649. Anal. Calcd. for C₃₄H₄₀N₆: C, 76.66; H, 7.57; N, 15.78. Found: C, 76.91; H, 7.87; N, 15.36.

2. Characterization: General Procedures and Experimental Details

X-ray Crystallography: Single-crystal X-ray diffraction data for $[\text{RuCp}^*\text{mes}]^+\Gamma^-$ and $[\text{N-DMBI}]^+\text{PF}_6^-$ were collected on a Bruker SMART APEX II CCD diffractometer (graphite-monochromatized Mo K α radiation with $\lambda = 0.71073 \text{ \AA}$, ω and ϕ scan mode) at 100 K and were corrected for absorption using the SADABS program.^[S14] The crystal structures were solved by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. All Hydrogen atoms were geometrically placed and refined using a riding model. Crystal and refinement parameters are summarized in Table S1. The crystallographic data may be obtained in CIF format from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk); the deposition numbers for the two structures are CCDC 1886261 and 1886262, respectively.

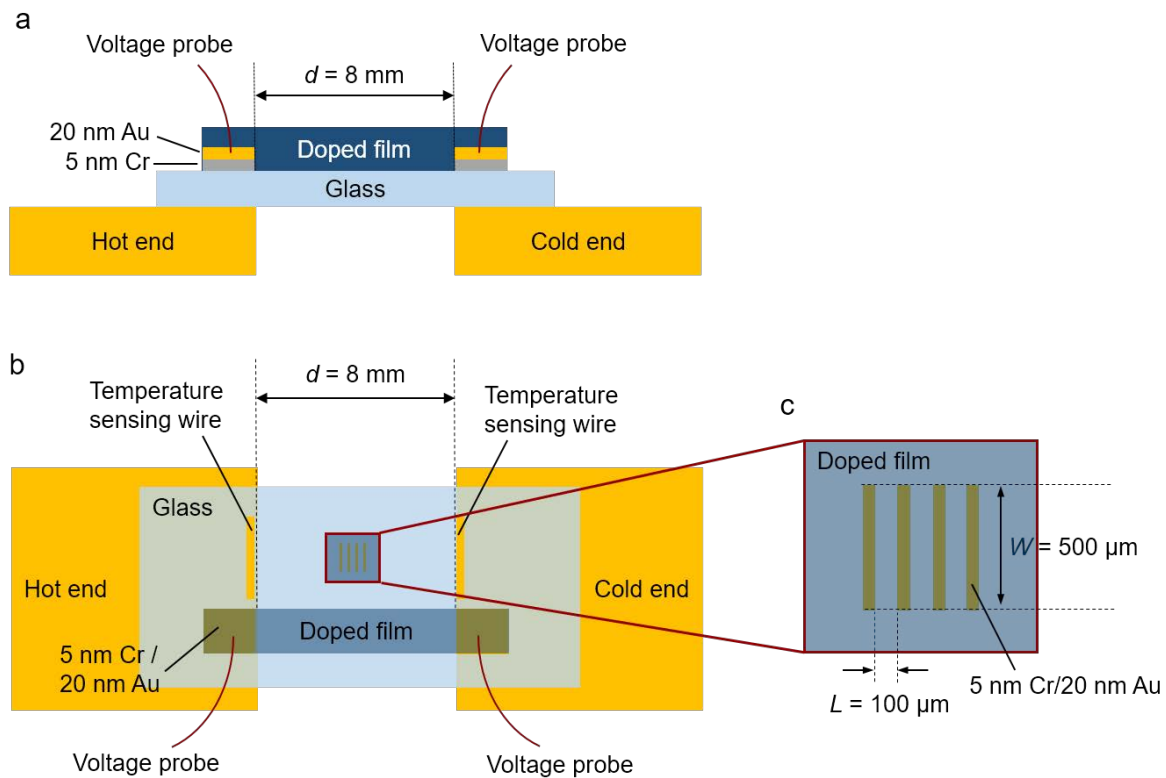
Absorption Spectroscopy: Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis-NIR spectrometer. The samples were encapsulated to avoid exposure to ambient air during measurement.

Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS): The GIWAXS data were recorded at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2396 $\text{\AA}$. BL14B1 is a beamline based on bending magnet and a Si (111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection.

Atomic Force Microscopy (AFM) and Scanning Kelvin Probe Microscopy (SKPM): AFM and SKPM studies were performed with a Cypher atomic force microscope (Asylum Research, Oxford Instruments). The surface morphology and the potential mappings were also recorded with a scan rate of 2 $\square$ 3 Hz at AC mode (noncontact mode). Data analysis was performed by Igor Pro (Wavemetrics Inc., OR) software.

Device Fabrication, Conductivity and Seebeck Coefficient Measurements: The doping method used in this study was solution blending. FBDPPV were dissolved in anhydrous toluene (3 mg mL^{-1}) at 70°C overnight prior to using. FBDPPV solution was blended with dopant solutions as a function of doping ratio at room temperature. All devices for conductivity and Seebeck coefficient measurements were fabricated using glass substrates. The 20 nm thickness of gold layer (with 5 nm Cr adhesion layer) as electrodes were pre-patterned by photolithography on the glass with a channel length of $100 \text{ }\mu\text{m}$ and a channel width of $500 \text{ }\mu\text{m}$ as contact pad. Prior to use, the substrates were cleaned with acetone, cleaning agent, deionized water (three times) and isopropanol under ultrasonics, and then were dried with a nitrogen flow. Doped thin films were deposited on the cleaned substrates by spin-coating at 1500 rpm for 30 s, and then annealed at 120°C for 8 h for the hydride dopant N-DMBI-H, and 80°C for 15 min for the dimer dopants $(\text{RuCp}^*\text{mes})_2$ and $(\text{N-DMBI})_2$. The conductivity (resistance) was collected by four-probe measurement in a N_2 glove box with Keithley 4200 SCS semiconductor parameter analyzer. The film thickness (ca. 20 nm) was determined by AFM. The Seebeck coefficient measurements were done in vacuum. The doped films for Seebeck measurements were deposited by the same procedures as those in conductivity measurements. The doped films were patterned to isolate the heater from the semiconductor and avoid electrical crosstalk with the thermal voltage probes and reduce the gate leakage current. The Seebeck coefficient is calculated by $S = \Delta V_{\text{therm}} / \Delta T$, where ΔV_{therm} is the thermal voltage between the hot and the cold ends of the device under a temperature difference, ΔT . Data were collected from 270 to 330 K. The ΔV_{therm} was monitored by Keithley 4200 SCS, and the temperature difference was introduced by Joule heat (heater) and a liquid-nitrogen cooling system. To accurately establish the temperature difference, ΔT , between the two contact pads, two temperature-sensing wires (5 nm Cr/20 nm Au bilayer) were introduced on the hot and the cold ends and were aligned with the patterned polymer

layer. The temperature coefficient of resistance (TCR) of the temperature sensing wires was calculated from the slope of the measured resistance versus temperature. The resistance of the metal wires is linear correlated with the temperature. TCR was found to be $0.307 \, \Omega \, K^{-1}$ with $R^2 = 0.9999$. By monitoring the resistance evolution of the temperature sensing electrodes, the accurate temperature of the contact pads was obtained by $T_h = T_{r.t.} + (R_h - R_{r.t.})/TCR$ and $T_c = T_{r.t.} + (R_c - R_{r.t.})/TCR$. The temperature difference was then given by the difference in temperature between the hot and the cold ends $\Delta T = T_h - T_c$. The device architecture for Seebeck coefficient measurements is shown as following:



Polaron Interaction Model: Please see Figure S10.

Comparison to Kang-Snyder Model: Please see Figure S11.

Ultraviolet Photoemission Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS): XPS and UPS were conducted on a Kratos AXIS AXIS Supra/Ultra Photoelectron Spectrometer under an ultrahigh vacuum of about 3×10^{-9} Torr with an unfiltered He I gas discharge lamp source (21.22 eV) and a monochromatic Al $K\alpha$ source (1486.7 eV, $\theta = 90^\circ$) as

the excitation source, respectively. Al $K\alpha$ source operated at 14 kV and 15 mA. The instrumental energy resolution for UPS and XPS were 0.1 eV and 0.5 eV, respectively. Data analysis was performed by CasaXPS software. For sample preparation, all films were deposited on heavily doped n-type Si wafers in a N₂ glove box and transferred through a transport system without air exposure into the spectrometer analysis chamber.

3. Figure S1–S15 and Table S1–S2

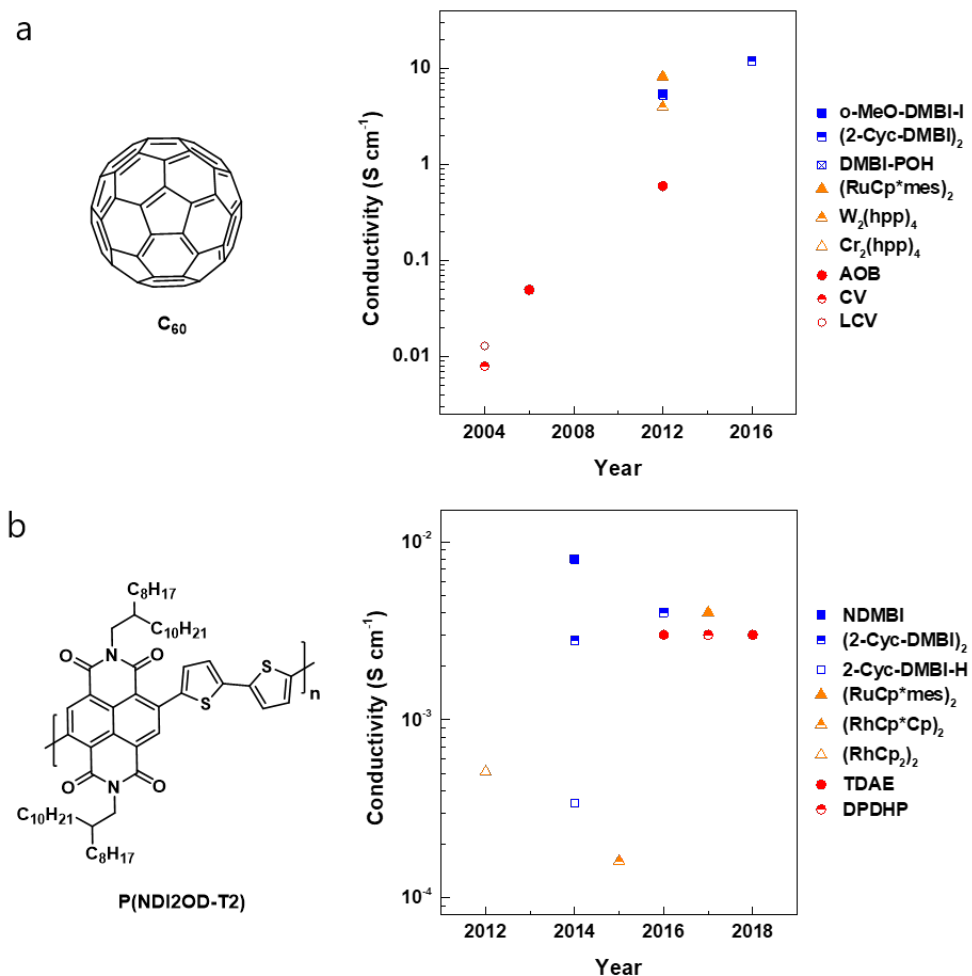


Figure S1. Summary of reported electrical conductivities of doped C_{60} a) and P(NDI2OD-T2) b) systems as a function of dopant. Chemical structures of dopants can be found in Figure S2.

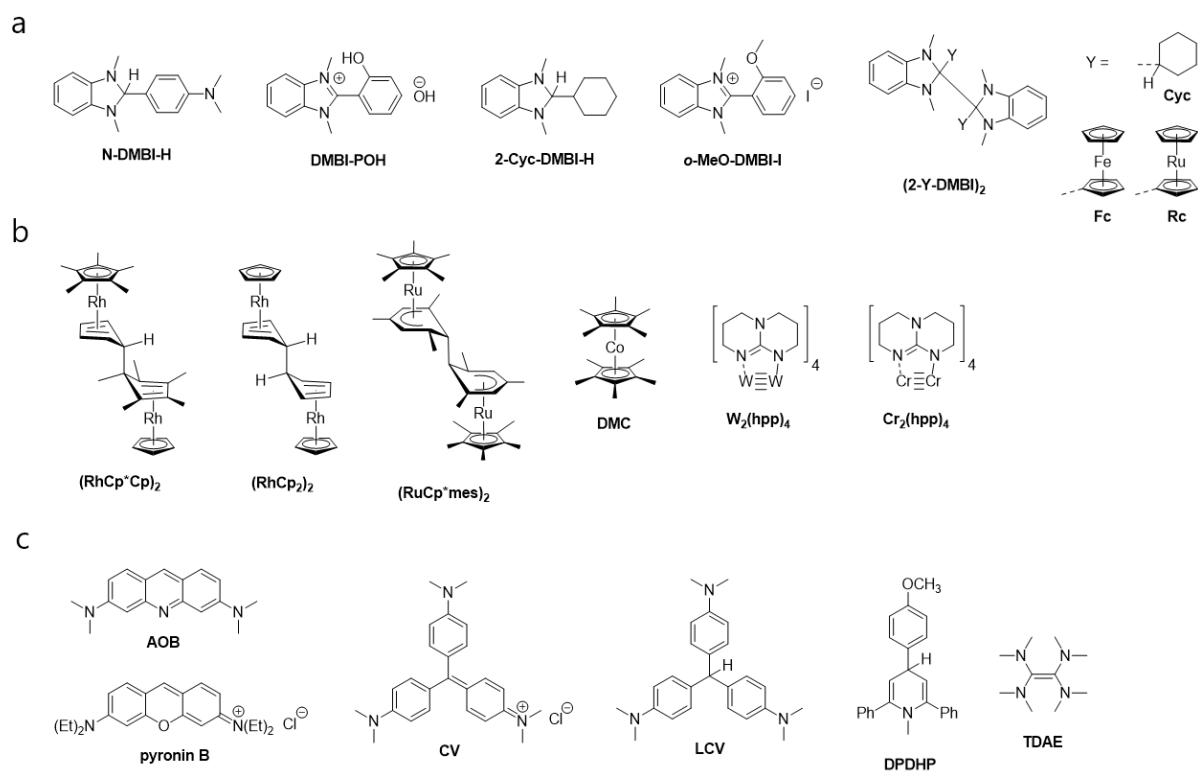


Figure S2. Reported n-dopants that used in molecular doping for organic semiconductors. a) DMBI derivatives; b) organometallic and metal-organic compounds; c) other classes.

Table S1. Crystal and structural refinement data for [RuCp*mes]⁺I[−] and [N-DMBI]⁺PF₆[−].

	[RuCp*mes] ⁺ I [−]	[N-DMBI] ⁺ PF ₆ [−]
Empirical formula	C ₁₉ H ₂₇ IRu	C ₁₇ H ₂₀ F ₆ N ₃ P
FW	483.37	411.33
Crystal growth	Evaporation of CH ₂ Cl ₂ /Et ₂ O solution	Evaporation of acetone solution
Crystal appearance	Colorless prisms	Pale pink needles
Crystal system	Monoclinic	Monoclinic
Space group	<i>Cc</i>	<i>P2₁/n</i>
<i>a</i> / Å	8.833(6)	8.671(11)
<i>b</i> / Å	15.951(10)	7.448(9)
<i>c</i> / Å	14.286(9)	28.61(4)
β / °	101.164(8)	90.356(18)
<i>V</i> / Å ³	1975(2)	1848(4)
<i>Z</i>	4	4
ρ_{calc} / g cm ^{−3}	1.626	1.479
μ / mm ^{−1}	2.351	0.213
<i>F</i> (000)	952	848
θ range / °	2.939–31.713	2.846–45.684
Index ranges	−12 ≤ <i>h</i> ≤ 12, −23 ≤ <i>k</i> ≤ 23, −20 ≤ <i>l</i> ≤ 20	−9 ≤ <i>h</i> ≤ 9, −7 ≤ <i>k</i> ≤ 7, −30 ≤ <i>l</i> ≤ 30
No. reflns collected	9512	12290
No. Indep reflns	5482 [<i>R</i> _{int} = 0.0647]	2313 [<i>R</i> _{int} = 0.1102]
No. reflns <i>I</i> > 2 σ (<i>I</i>)	5053	1542
No. data/restraints/params	5482/116/198	2313/0/248
GOF (<i>F</i> ²)	1.077	1.030
<i>R</i> ₁ (<i>F</i>), <i>wR</i> ₂ (<i>F</i> ²) [<i>I</i> > 2 σ (<i>I</i>)]	0.0620, 0.1616	0.0654, 0.1809
<i>R</i> ₁ (<i>F</i>), <i>wR</i> ₂ (<i>F</i> ²) [all data]	0.0677, 0.1660	0.1103, 0.2453
Largest peak, hole / e Å ^{−3}	2.427, −2.899	0.62, −0.96

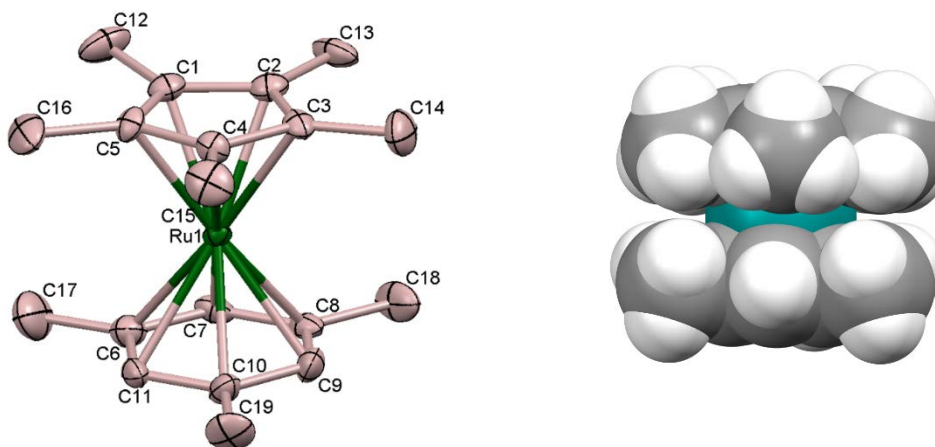


Figure S3. Molecular structure of $[\text{RuCp}^*\text{mes}]^+$ from the crystal structure of its iodide salt (left, 50% thermal ellipsoids, hydrogen atoms excluded for clarity; right, space-filling representation). Selected geometric parameters: $\text{Ru}-\text{C}_{\text{Cp}^*}$, 2.179(13)–2.206(11) Å (av., 2.195 Å); $\text{Ru}-\text{C}_{\text{mes}}$, 2.218(12)–2.237(12) Å (av., 2.227 Å); $\text{Ru}-\text{Ct}_{\text{Cp}^*}$, 1.821(5) Å; $\text{Ru}-\text{Ct}_{\text{mes}}$, 1.715(5) Å; $\text{Ct}_{\text{Cp}^*}-\text{Ru}-\text{Ct}_{\text{mes}}$, 179.5(2)° (Ct_{Cp^*} and Ct_{mes} denote the centroids of the Cp^* and mesitylene rings, respectively). These values are similar to those seen for other $[\text{RuCp}^*(\text{arene})]^+$ salts.^[S15]

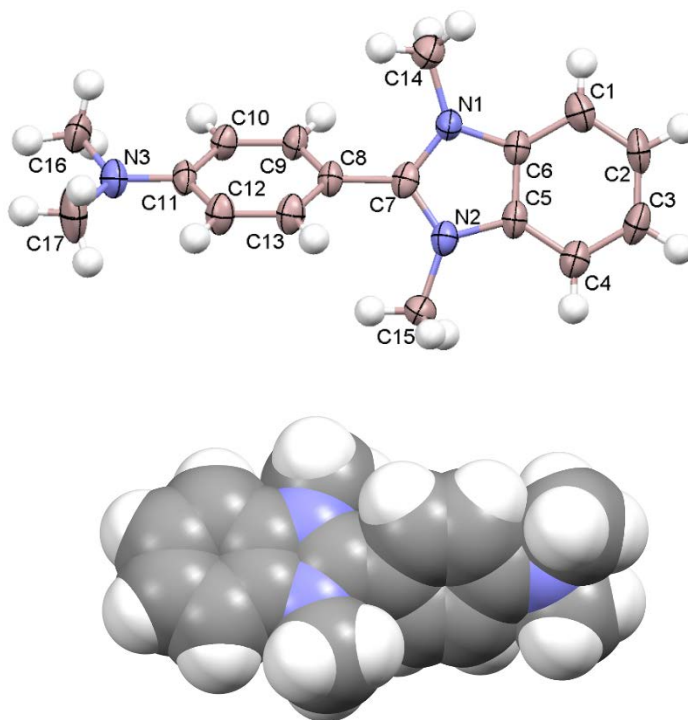


Figure S4. Molecular structure of $[\text{N-DMBI}]^+$ (top, 50% thermal ellipsoids; bottom, space-filling representation) from the crystal structure of its hexafluorophosphate salt. Selected geometric parameters: $\text{N1}-\text{C6}$, 1.390(7) Å; $\text{N1}-\text{C7}$, 1.360(7) Å; $\text{N2}-\text{C5}$, 1.398(7) Å; $\text{N2}-\text{C7}$, 1.352(7) Å; $\text{N3}-\text{C11}$, 1.362(6) Å; $\text{C1}-\text{C6}$, 1.391(8) Å; $\text{C1}-\text{C2}$, 1.352(9) Å; $\text{C2}-\text{C3}$, 1.401(9) Å; $\text{C3}-\text{C4}$, 1.374(8) Å; $\text{C4}-\text{C5}$, 1.390(8) Å; $\text{C4}-\text{C5}$, 1.390(8) Å; $\text{C5}-\text{C6}$, 1.385(8) Å; $\text{C7}-\text{C8}$, 1.446(7) Å; $\text{C8}-\text{C9}$, 1.391(8) Å; $\text{C8}-\text{C13}$, 1.397(8) Å; $\text{C9}-\text{C10}$, 1.366(7) Å;

C10—C11, 1.412(7) Å; C11—C12, 1.405(8) Å; C12—C13, 1.362(8) Å; plane_{C1-C7,N1-N2}/plane_{C8-C13} angle, 52.6°. The interplanar angle falls within the range seen for other 1,3-dialkyl-2-aryl-1*H*-benzo[*d*]imidazolium structures (42.0-60.5° for examples without *ortho* substituents that lead to greater twisting).^[S16] Note that values for three different 1,3-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazolium salts range from 42.0–54.9°,^[S16a-c] i.e., depend on crystal packing as well as the cation itself. Bond lengths are also similar.

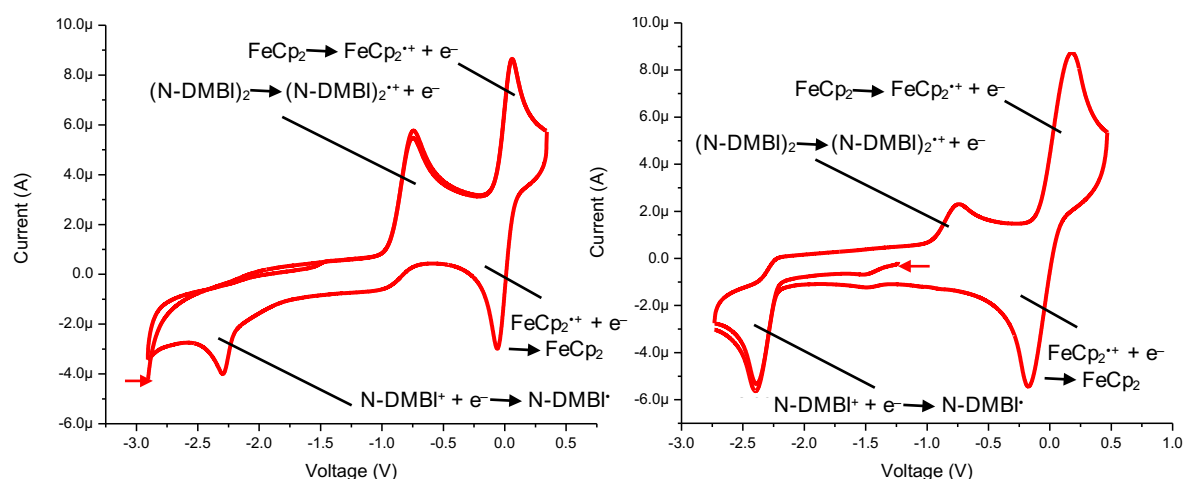


Figure S5. Cyclic voltammograms of (N-DMBI)₂ (left) and of N-DMBI⁺PF₆[−] (right) in THF/0.1 M nBu₄NPF₆, both containing ferrocene as an internal reference. The red arrows indicate the initial potentials and scan directions. In common with other DMBI-based with different 2-substituents,^[S8] (N-DMBI)₂ exhibits an irreversible oxidation wave in its cyclic voltammogram and the reduction of the corresponding monomer cation is seen following scanning of this oxidation. Similarly the oxidation of the dimer is seen in the voltammogram of DMBI⁺ following reduction of the cation. The peak oxidation potential of −0.75 V vs. FeCp₂⁺⁰ falls within the range reported for other DMBI dimers. The effective redox potential of the dimer, $E(D^+/0.5D_2)$, will depend on both the monomer potential (−2.38 V) and the strength of the C—C bond in the dimer ($E(D^+/0.5D_2) = E(D^+/D) - 0.5 \square G_{\text{diss}}(D_2)$);^[S3,S9] if the latter is assumed to be the same as that previously determined for (Fc-DMBI)₂,^[S9] $E(D^+/0.5D_2)$ would be ca. −2.0 V. In any case, reduction of TIPS-pentacene to its radical anion indicate that $E(D^+/0.5D_2)$ for (N-DMBI)₂ is at least as reducing as −1.45 V (Figure S6).

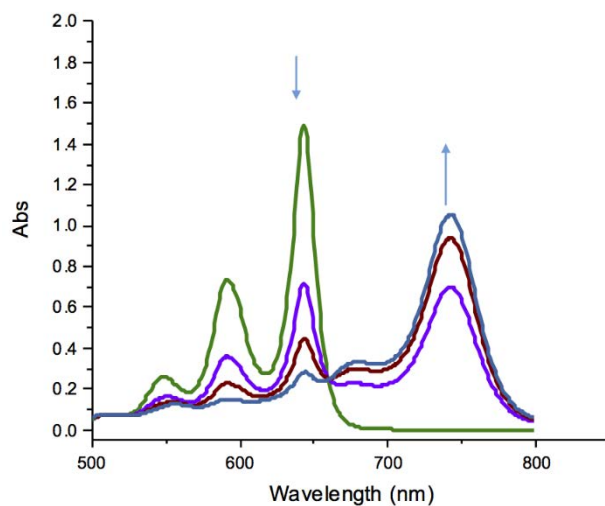


Figure S6. UV-*vis*-NIR absorbance spectra in toluene of TIPS-pentacene before (black) and after (blue) addition of (N-DMBI)₂. The peak at ca. 750 nm is attributable to TIPS-pentacene^{•−}.^[S6] Reduction of TIPS-pentacene to its radical anion indicate that $E(D^+/0.5D_2)$ for (N-DMBI)₂ is at least as reducing as −1.45 V.

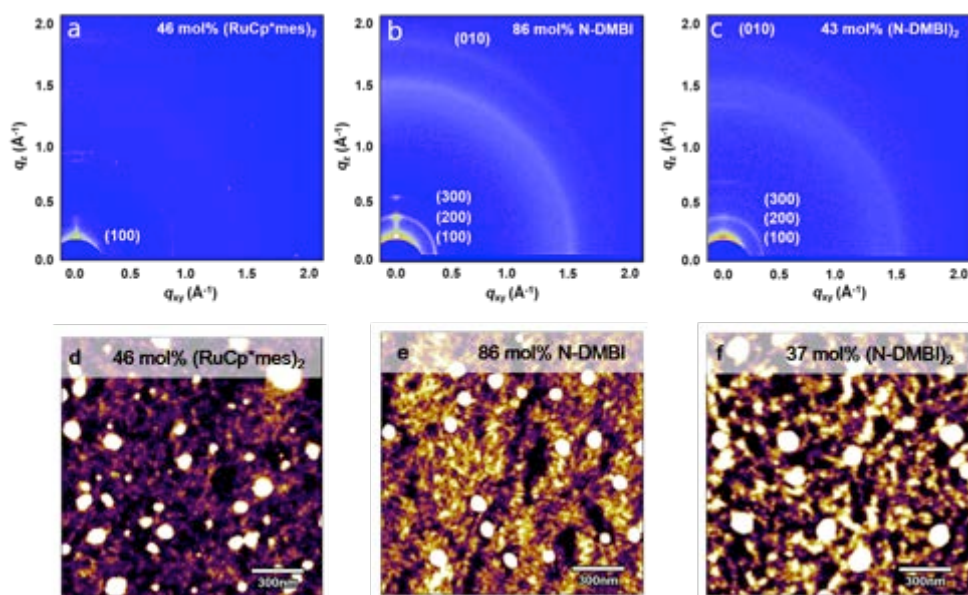


Figure S7. GIWAXS a)-c) and AFM d)-f) images for excess doping level as functions of dopant. The molar ratio of dopants is shown in inset.

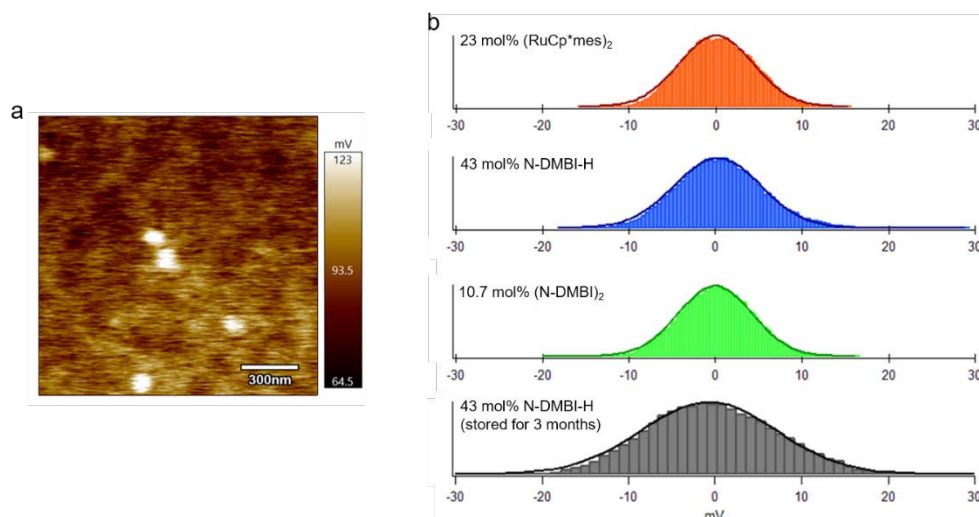


Figure S8. a) After the doped film with 43 mol% N-DMBI-H was stored for 3 months, in contrast to Figure 5g-i, the potential mapping became inhomogeneous and thus showed phase separation. b) Extracted from potential mappings, the distribution of potential contrast of the aging film was broader than those of homogeneous films (Figure 5g-i). The narrow distributions with similar shapes (the top three) are indicative of good miscibility (no obvious phase separation) in all optimally-doped films. To better compare the width of distribution, the mean was redefined to as zero potential. Gaussian distribution best fits all distributions.

Polaron Interaction Models: Using the Seebeck coefficients and known dopant concentrations, polymer-dopant systems were compared with Seebeck coefficient models that account for the impact of charge carrier interactions on the entropy of mixing.^[S18] Figure S10a shows the full range for Seebeck coefficients and its ability to change from positive to negative as a function of doping. Figure S10b shows the absolute Seebeck coefficient of the studied systems assuming that each dopant dopes the polymer backbone, produces a charge carrying species that contributes to charge transport, and that dimers only contribute $1e^-$. Figure S10c shows the results if each dimer dopant contributes $2e^-$. Nearest Neighbor Interactions accounted for only second neighbors ($b = 2$). Using these models in future studies, with more robust methods of measuring dopant efficacy, could lead to optimized Seebeck coefficients based on polaronic interaction engineering.

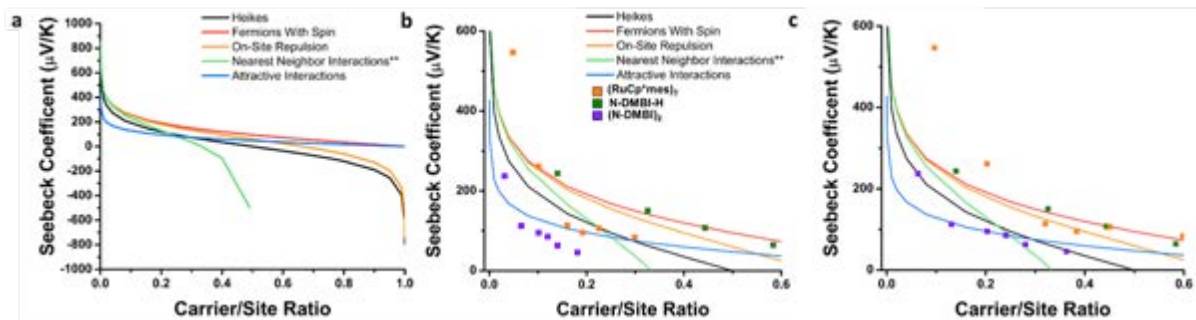


Figure S9. Seebeck coefficient dependence on carrier concentration and models (lines) experimentally measured and extrapolated and values (squares). (a) General models, (b) absolute value of the Seebeck coefficients measured in this study assuming a complete $1e^-$ transfer, (c) absolute value of the Seebeck coefficients measured in study assuming a complete $2e^-$ transfer for dimer dopants.

Comparing to the Kang-Snyder Model: Different s values could be understood as different transport pathways. $s = 2$ best fits the benzoimidazole systems based on linear regressions, but $s = 3$ may also be appropriate based on visual interpretations. s is a transport exponent and $s = 3$ is possible if ionized impurities are the dominant scattering mechanism for charge carriers.^[S13a] Because s may equal 2 for benzoimidazole systems (definitively less than 3), it could indicate that benzoimidazole dopants scatter charge carriers differently.

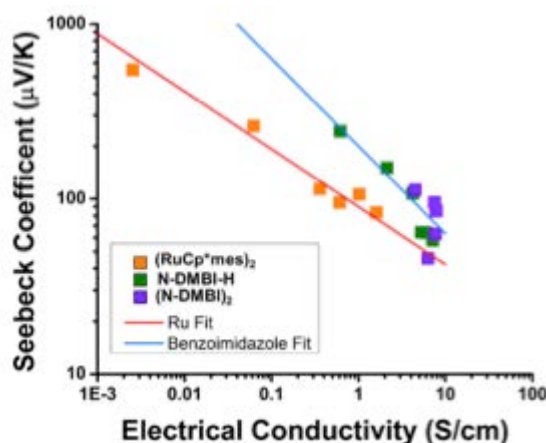


Figure S10. S - σ plot for Kang-Snyder model evaluations. For the $(\text{RuCp}^*\text{mes})_2$ system, a $k = 90$ and a $s = 3$ were used. For the benzoimidazole systems, a $k = 200$ and a $s = 2$ were used. $S \propto k\sigma^{1/s}$. The vertical series of benzoimidazole dimer data points are associated with over-doped polymer.

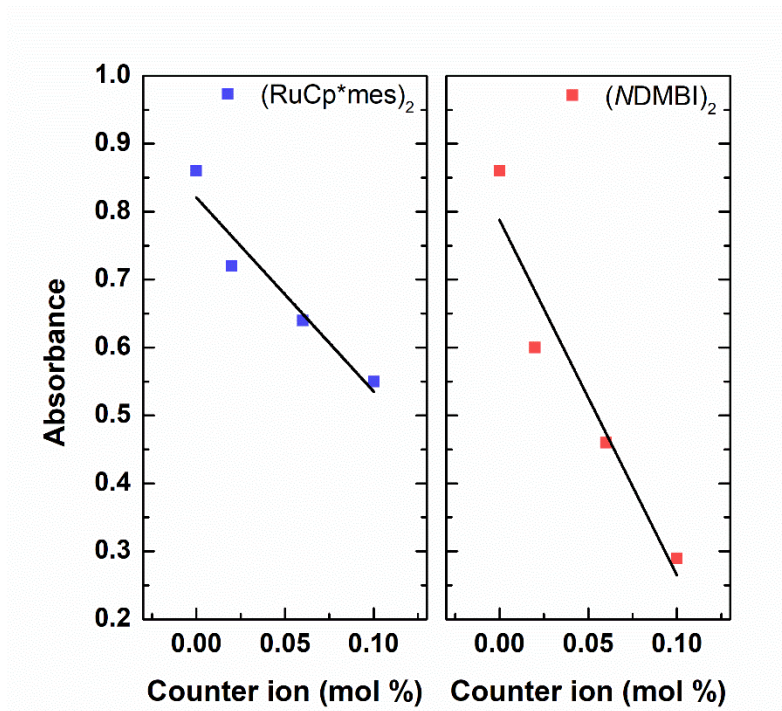


Figure S11. Solution absorbances at 786 nm of (RuCp*mes)₂- and (N-DMBI)₂-doped FBDPPV as a function of dopant concentration. The absorbance shown here is extracted with peak deconvolution and fitting at 786 nm as that attributable to the 0-0 transition of the neutral FBDPPV.^[S1] To better compare the quenched repeat unit/counter ion ratio, what shown here is the concentration of counterion rather than dopant concentration. The effective redox potentials for the two dimers, $E(D^+/0.5D_2)$, are required to demonstrate that at equilibrium no unreacted dopant remains in the UV-vis-NIR doping experiments. As discussed in the caption for Figure S5, $E(D^+/0.5D_2)$, will depend on both the monomer potential and the strength of the C—C bond in the dimer.^[S3,S9] However, both readily reduce TIPS-pentacene in solution, which has a much lower electron affinity (3.0 eV from inverse photoelectron spectroscopy; estimated at ca. 3.4 eV from electrochemistry) than the FBDPPV (estimated at ca. 4.2 eV from electrochemistry).^[S1,S6] Additionally, at room temperature the change in absorbance of our doped systems was complete in seconds; therefore, it is reasonable to assume that at low doping concentrations, the reactions between FBDPPV and (RuCp*mes)₂ or (N-DMBI)₂ is quantitative if the reaction is observed to reach equilibrium. After extracting the absorbance with peak deconvolution and fitting, the evaluated delocalization lengths are 2.9 repeat units for FBDPPV-(RuCp*mes)₂ system and 5.2 repeat units for FBDPPV-(N-DMBI)₂ system.

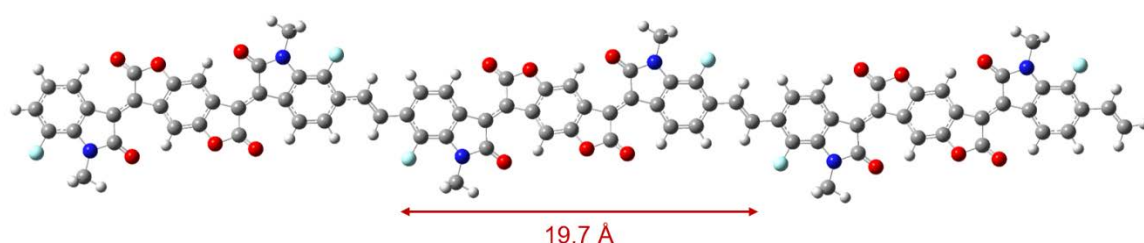


Figure S12. Optimized molecular structure of trimer FBDPPV radical anion ($n = 3$). The length of a repeat unit is almost 19.7 Å (UB3LYP/6-31G(d)).

To further deconvolute the impacts of dopant cation on structure and electrical conductivity of doped FBDPPV, precise optical absorption spectra were collected, both at low doping concentrations. The extent of optical bleaching of the neutral polymer absorption by each electron is indicative of the polaron delocalization length.^[S17] Such a method has been employed in classic conjugated polymer (such as P3HT)^[S17b] and in D-A copolymers (such as PDI- and NDI-based polymers),^[S17a] and has been successfully used to explain structure-property relationships. When using the two dimers (RuCp*mes)₂ and (N-DMBI)₂ as n-dopants, at low doping concentration and equilibrium, it is anticipated that no unreacted dopant remains in the solution; therefore, we estimate the polaron delocalization length to be 2.9 and 5.2 repeat units for the (RuCp*mes)₂ and the (N-DMBI)₂ systems respectively, corresponding to 5.7 and 10.2 nm, and indicating that the polarons in the RuCp*mes⁺ system are more localized than those in polymer with N-DMBI⁺ cations, consistent with the trends seen in electrical conductivities.

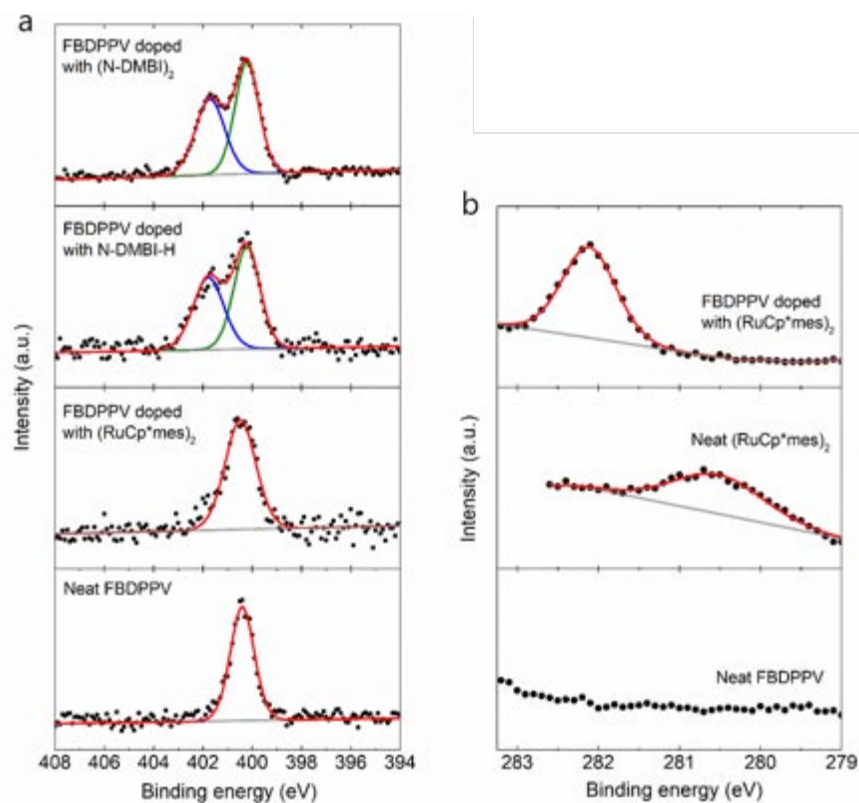


Figure S13. a) XPS N 1s spectra of undoped FBDPPV, and FBDPPV doped with 23mol% (RuCp*mes)₂, 43 mol% N-DMBI-H, 10.7 mol% (N-DMBI)₂, and b) XPS Ru 3d^{5/2} spectra of neat FBDPPV, neat (RuCp*mes)₂ and FBDPPV doped with 23 mol% (RuCp*mes)₂. The peaks that emerge at around 402 eV are attributable to N-DMBI⁺ cation (Figure S13a).^[S10a] Although polymer FBDPPV was blended with a lower dopant ratio of (N-DMBI)₂ (10.7 mol%) than of N-DMBI-H (43 mol%), the (N-DMBI)₂-doped FBDPPV system showed a visually higher ratio of cation (around 402 eV) to polymer and neutral dopant (around 400 eV) than FBDPPV doped with N-DMBI-H. As a result, it is reasonable to believe that (N-DMBI)₂ has a higher doping efficiency than N-DMBI-H. On the other hand, the absence of signal at around 281.3 eV that corresponds to the Ru 3d orbital in (RuCp*mes)₂ and the presence of signal at around 282.2 eV that corresponds to the lower-electron density Ru 3d orbital in RuCp*mes⁺ reveal that (nearly) all (RuCp*mes)₂ became RuCp*mes⁺.^[S10b]

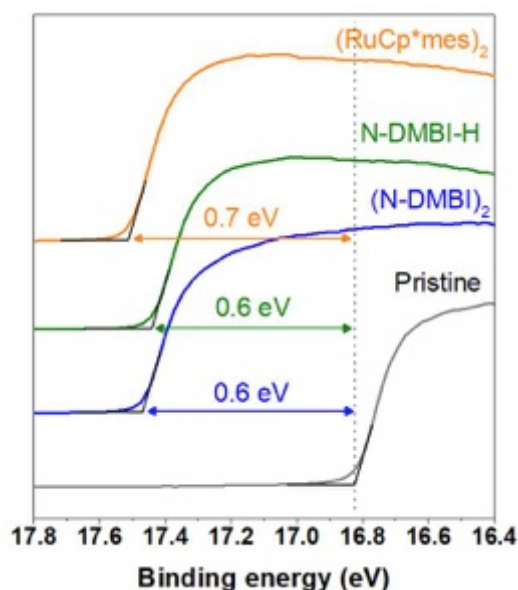


Figure S14. UPS data of the undoped FBDPPV, and the FBDPPV doped with 23 mol% (RuCp*mes)₂, 43 mol% N-DMBI-H, and 10.7 mol% (N-DMBI)₂, showing a larger Fermi level shift in the (RuCp*mes)₂ system than in N-DMBI-H and (N-DMBI)₂ systems.

Table S2. Summary of energy levels collected by UPS for FBDPPV with (RuCp*mes)₂, N-DMBI-H, and (N-DMBI)₂, respectively.^[S12]

System	Secondary Electron Cutoff Binding Energy [eV] ^{a)}	Fermi Level [eV] ^{b)}	HOMO Edge [eV] ^{c)}	HOMO Level [eV] ^{d)}
Neat FBDPPV	16.8	4.4	2.0	6.4
23 mol% (RuCp*mes) ₂	17.5	3.7	2.3	6.0
43 mol% N-DMBI-H	17.4	3.8	2.3	6.1
10.7 mol% (N-DMBI) ₂	17.4	3.8	2.3	6.1

^{a)} Secondary Electron Cutoff energy was extracted from raw UPS data, with the Fermi Level aligned to 0 eV.

^{b)} The incident energy is 21.22 eV and the secondary Electron Cutoff energy was 16.8 eV (pristine), so all graphically obtain values for the pristine film were then shifted by 4.4 eV such that the cutoff energy is representative of the vacuum energy level for the film sample. When measuring, the Fermi level was aligned to 0, but after secondary electron cutoff shifting, we determine the pristine Fermi level is 4.4 eV lower (more stable) than the vacuum level.

^{c)} The HOMO edge value was measured to be at 2.0 eV below the Fermi level, where the signal intensity dramatically increased and indicative of the valence band.

^{d)} After the shift, we determine the HOMO level for the pristine sample to be 6.4 eV below vacuum level. Similar procedures were applied to subsequent systems.

UPS was performed on FBDPPV films doped with the highest electrical conductivity (23 mol% (RuCp*mes)₂, 43 mol% N-DMBI-H, and 10.7 mol% (N-DMBI)₂) to better understand how doping impacted the electronic states. Table S2 shows the characteristic energy levels derived from the UPS measurements.^[S12] The presence of additional negative charge carriers due to doping is evident by the upward (less stable) shift in the chemical potential. The upward shift of the chemical potential is indicative that doping creates charge carriers and donor states closer to the conducting energy states, and the shift of the chemical potential for the (RuCp*mes)₂ system is ca. 100 meV greater than N-DMBI-H and (N-DMBI)₂ systems.

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