Molecular Descriptor and Criterion for Efficient N-Doping of Organic Semiconductors

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Abstract

Precursor dopants have been extensively applied for n-doping of organic semiconductors (OSCs) to address the trade-off between dopant reducibility and stability. N-DMBI-H derivate is believed as one of the most successful air-stable n-dopants. Two doping mechanisms, i.e., hydrogen atom transfer (HAT) and hydride transfer (HYT), have been suggested but the dominance of them remains controversial. In this work, we rationalize the thermodynamics and kinetics of HAT and HYT reactions between N-DMBI-H derivate and a variety of OSCs and conjugated polymers based on the density functional theory, and manifest that the HYT via concerted electron and hydrogen atom transfer is the most viable doping mechanism.

We find two linear relations between the free energy change of HYT, ∆GHYT, and the electron affinity (EA) of OSCs as well as the ionization energy (IE) of dopant radicals, D⁻, and the Brønsted-Evans-Polanyi relation between the ∆GHYT and the activation barrier of HYT, ∆G‡. By correlating important thermodynamic and kinetic parameters of HYT to facile properties of OSCs and dopants, molecular descriptors of n-doping are uncovered. Furthermore, an EA(OSC) – IE(D⁻) > 1.0 eV criterion is proposed for achieving a high doping efficiency based on the requirement ∆GHYT < 0. Finally, new quinoid-structure polymers with EA > 4.0 eV and good backbone planarity are designed as potential n-type OSCs. The molecular descriptors and criterion discovered provide a simple and operable way to speed up the development of n-type OSCs and dopants by high-throughput screening and machine learning techniques.

Keywords: Organic semiconductors; N-doping; Conducting polymers; Hydride transfer
1. Introduction

Organic semiconductors (OSCs) are eco-friendly, flexible, economic, and non-toxic, and they possess low thermal conductivities, which brings extensive applications in next-generation portable electronic devices, including organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic electrochemical transistors (OECTs), as well as organic thermoelectric (OTE) devices.\(^1\)-\(^8\) Electrical conductivity (\(\sigma\)) is an essential property of OSCs. So far, the \(\sigma\) of p-type and n-type OSCs are ca. \(10^4\) S/cm and \(10^3\) S/cm, respectively.\(^8\)-\(^12\) However, except for a very recently reported n-type polymer that shows ultrahigh \(\sigma\) over 2000 S/cm,\(^11\) n-type OSCs rarely show electrical conductivities over 100 S/cm.\(^13\)-\(^16\) Hence, the development of n-type OSCs still lags behind the p-type ones, and studies on improving the \(\sigma\) of n-type OSCs are urgently needed. Controllable chemical doping based on redox reactions is one of the most effective strategies to tune the \(\sigma\) of OSCs.\(^17\),\(^18\) However, n-doping is usually more challenging than p-doping mainly due to the conflict between doping activity and stability of n-dopants.\(^19\) For efficient electron transfer (ET), the ionization energy (IE) of n-dopants should be smaller than the electron affinity (EA) of OSCs, which reduces the air stability of n-dopants.\(^17\)-\(^22\) Many efforts have devoted to exploiting air-stable n-dopants, which are usually stable at room temperature (RT) while active when heated or under radiation.\(^23\)-\(^32\) Among the air-stable n-dopants, benzimidazole (BI) derivatives, especially 1,3-Dimethyl-2-(4-(dimethylamino)phenyl)-2,4-dihydro-1H-benzimidazole, N-DMBI-H (see Fig. 1 and Fig. S1), is believed to be the most popular and successful one owing to its good stability and solution processability.\(^17\),\(^33\) It has been applied to dope broad types of semiconductors including inorganics and organics.\(^34\)-\(^40\) By doping with N-DMBI-H, the \(\sigma\) of OSCs can be increased by orders of magnitude. However, the doping efficiency, which is defined as the ratio between the number of mobile charge carriers after doping and the number of dopant molecules,\(^17\) is generally on the order of 10\%.\(^15\),\(^22\) Besides, the doping mechanism of N-DMBI-H and its derivates is not well understood and remains controversial,\(^17\) which hinders the improvement of doping efficiency.

The IE of N-DMBI-H is up to 4.7 eV,\(^41\) which is higher than the EA of most OSCs.
As a result, the direct ET from N-DMBI-H to OSCs is usually energetically unfavorable, though it may occur for a few strongly oxidizing cases. Nevertheless, its dehydrogenated neutral radical N-DMBI· is very reductive; the singly occupied molecular orbital (SOMO) level is calculated to be ca. ~-2.4 eV\textsuperscript{34,41-43} or ~-2.8 eV\textsuperscript{28,44} depending on the method. Therefore, the C-H bond activation process to form N-DMBI· that can reduce OSCs was first proposed\textsuperscript{33} and it was supported by the primary kinetic isotope effect (KIE) experiment.\textsuperscript{41,45} However, the standard enthalpy changes of the C-H bond homolysis and heterolysis were calculated to be more than +70 kcal/mol,\textsuperscript{43} which are extremely hard to occur even under heating. In addition, the kinetics of the doping reaction have been revealed as second-order, namely, the rate constant relies on the concentrations of both N-DMBI-H and OSC, which indicates that the rate-determining steps (RDSs) of doping processes are bimolecular.\textsuperscript{41} Hence, the hydrogen atom transfer (HAT) and (or) hydride (hydrogen anion) transfer (HYT) between dopants and OSCs are widely recognized RDSs in recent years.\textsuperscript{17} As displayed in Fig. 1a, the HAT and HYT can be expressed as Eq. (1) and Eq. (2), respectively, where D and A represent the dopant and OSC, correspondingly.

\[
\begin{align*}
\text{DH} + \text{A} & \rightarrow \text{D}^- + \text{AH}^- \\
\text{DH} + \text{A} & \rightarrow \text{D}^+ + \text{AH}^-
\end{align*}
\]

Because D· is strongly reductive, after HAT, it will convert into D+ immediately through ET,

\[
\text{D}^- + \text{A} \rightarrow \text{D}^+ + \text{A}^-
\]

Recent results show that in most cases, the formed AH\textsuperscript{-} or AH\textsuperscript{-} can rapidly convert into A\textsuperscript{-},\textsuperscript{45} which should be the main conducting species in the doped film. The ET between AH\textsuperscript{-} and A after HYT has been proposed:

\[
\text{AH}^- + \text{A} \rightleftharpoons \text{AH}^- + \text{A}^-
\]

The absence of hydrogenated species in the doped film reported before indicates the hydrogen radical may eventually release as H\textsubscript{2} through Eq. (5) or Eq. (6).\textsuperscript{45}

\[
\begin{align*}
2\text{AH}^- & \rightarrow 2\text{A} + \text{H}_2 \\
\text{AH}^- + \text{DH} & \rightarrow \text{A} + \text{D}^- + \text{H}_2
\end{align*}
\]

After Eq. (6), the ET process in Eq. (3) occurs to form D\textsuperscript{+} and A\textsuperscript{-}. The succeeding
reactions of Eq. (1) and Eq. (2) are either ET or radical-involved, which are reasonably fast. Hence, the HAT and (or) HYT are considered as the RDSs of the doping process.

However, it is hard to distinguish them by experiments due to the rapid successive reactions and the same final products. Recently, Marder and coworkers showed that for fullerene and some imide- or amide-containing small-molecule OSCs, the HYT is less endergonic than the HAT, and the reaction rates vary greatly for different OSCs.\textsuperscript{45} Besides, there are many reports showing distinctive doping behaviors and efficiencies when using N-DMBI-H to dope OSCs with similar structures.\textsuperscript{13, 14, 34, 46, 47} These interesting results are still not well understood. Besides, comprehensive studies on the dominance of HAT and HYT as well as the underlying relations between molecular structure, the doping mechanism, and efficiency are still lacking. Hence, detailed investigations are urgent to uncover the dominant RDS and help understand the n-doping of OSCs.

In this work, we systematically study the doping reaction between N-DMBI-H and its derivates and commonly used OSCs by using the density functional theory (DFT). We focus on the two reactions, i.e., HAT and HYT, and try to find the relation between the doping mechanism and the molecular structure of dopants and OSCs. By rationally analyzing the thermodynamics and kinetics of the reactions, examining the electronic structure of activated complexes, and comparing the $\Delta G^\ddagger$ and KIE with available experiments, we demonstrate that the HYT via concerted ET and HAT is the most favorable RDS for n-doping of OSCs. In addition, the linear relationships between the electron transfer driving force $\Delta = EA(\text{OSC}) - IE(D^\cdot)$ and $\Delta G_{\text{HYT}}$ are observed and discussed, and a criterion of $\Delta > 1.0$ eV for high doping efficiency is suggested. On top of that, four quinoid-structure polymers with large EAs and good planarity are designed as potential candidates for n-type OSCs. These results have significant implications for the understanding of the n-doping mechanism of OSCs and can guide the molecular design of both dopants and OSCs to reach a high doping efficiency.
2. Computational Methods

The geometry optimization, zero-point energy (ZPE), and thermodynamic corrections were obtained at the (U)B3LYP/6-31G** level of theory. All single-point energies were calculated at the (U)M06-2X/6-311+G** level of theory. The polarizable continuum model was used to mimic the solvent environment. Chloroform ($\varepsilon = 4.7$) was chosen as the solvent for its moderate polarity, which is close to OSCs. The intermolecular interactions in bimolecular systems were considered by using Grimme’s D3 correction.\textsuperscript{48} For OSCs, the optimal (lowest energy) hydrogen atom/hydride adsorption sites were searched at the (U)B3LYP/6-31G** level of theory. All sidechains were replaced by methyl groups to save the computational cost. Besides, only monomer,
dimer, and trimer were modeled for polymers, and the result of the trimer was used to represent that of the polymer. The oligomer chains of polymers were end-capped with -CH$_3$ or =CH$_2$ depending on the backbone structure (see Fig. S2 in Supporting Information). Frequency calculations were performed to check for the geometry optimization except in the search for favorable hydrogen/hydride addition sites. All the DFT calculations were performed using the Gaussian16 software package.$^{49}$ The molecular orbital localization analysis was performed using the Multiwfn code.$^{50}$ The corrections to thermodynamic functions at 298.15 K and 373.15 K were obtained by using the Shermo code$^{51}$ based on the output of Gaussian.

The $\Delta G$s of HAT and HYT reactions were calculated using Eq. (7) and Eq. (8), respectively, as follows

\[ \Delta G_{\text{HAT}} = G(D^+) + G(AH^+) - G(DH) - G(A), \]

\[ \Delta G_{\text{HYT}} = G(D^-) + G(AH^-) - G(DH) - G(A). \]

The most stable configurations of AH$^-$ and AH$^-$ were used to calculate the $G(AH^+)$ and $G(AH^-)$ (see Fig. S3 in Supporting Information). The Gibbs free energy of activation, $\Delta G^\dagger$, is defined as:

\[ \Delta G^\dagger = G(\text{TS}) - G(DH) - G(A). \]

The transition state (TS) of the reaction was calculated based on the UM06-2X/6-311+G**/UB3LYP/6-31G** level of theory, where the unrestricted DFT was used to consider the possible diradical configuration of TS in HAT. According to the results, the spin polarization effect was negligible. Hence, the restricted DFT was used for the analysis of the electronic structure of the activated complex along the intrinsic reaction path.

The KIE, $k_H/k_D$, was calculated using the transition state theory. The rate constant $k$ is given by$^{52}$

\[ k = \kappa \frac{k_B T}{h c^\Theta} \exp \left( -\frac{\Delta G^\dagger}{RT} \right), \]

where $\kappa$ is the transmission coefficient; $k_B$ is Boltzmann constant; $T$ is temperature; $h$ is the Plank constant; $c^\Theta$ is the standard molar concentration; $R$ is the ideal gas constant. Wigner’s correction$^{53, 54}$ for small tunneling was used to calculate the $\kappa$:
\[
\kappa = 1 + \frac{1}{24} \left( \frac{\hbar |\nu^\ddagger|}{k_B T} \right)^2,
\]

where \( \nu^\ddagger \) is the imaginary frequency of the transition state.

3. Results and Discussion

3.1 Thermodynamics of Hydrogen Atom Transfer and Hydride Transfer Reactions

To unveil the n-doping mechanism, 8 dopants and 52 OSCs including 25 small molecules and 27 polymers were systematically studied. The molecular structures were shown in Fig. 1 and Figs. S1-S2 in Supporting Information. The considered OSCs are either extracted from the literature or designed as model systems. They are grouped into 12 categories according to the backbone structures, including naphthalene diimide (NDI), perylene diimide (PDI), C60, benzodifurandione-based oligo(p-phenylene vinylene) (BDOPV), benzodifurandione-based poly(p-phenylenevinylene) (BDPPV), thiophene-fused benzodifurandione-based poly(p-phenylenevinylene) (TBDPPV), bis-isatin-based benzodifurandione-based poly(p-phenylenevinylene) (LPPV), bithiophene imide (BTI), thiophene-flanked diketopyrrolopyrrole (TDPP), pyridine-flanked diketopyrrolopyrrole (PyDPP), pyrazine-flanked diketopyrrolopyrrole (PzDPP), as well as thiophthene-flanked diketopyrrolopyrrole (TTDPP), see Fig. S4 in Supporting Information. The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are usually used to quantify the easies of losing and gaining an electron, respectively. Because the Kohn-Sham orbitals do not include the vibronic coupling, the adiabatic IE and EA, instead of the \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \), are calculated to compare the electron-donating capability of the dopants and the electron-accepting capability of the OSCs, respectively. The calculated EA of considered OSCs varies widely from 2.6 eV to 4.7 eV. The comparison with experiments is made in Table S1. Though the experimental EAs were measured by different research groups under different conditions, the calculations can still correctly reproduce the trend, and the mean absolute error (MAE) is only 0.19 eV, showing the reliability of the computational methods. By functionalizing the benzene ring of N-DMBI-H with different groups or end-capping the dihydro-benzimidazole with methyl
groups (structures are given in Fig. S1, Supporting Information), its doping activity can be tuned effectively. The calculated IE of DHs ranges from 4.9 eV to 5.2 eV, which is larger than the EA of all considered OSCs, suggesting that the direct ET from DH to OSCs is not favored. As expected, the IE of D· is from 2.7 eV to 3.1 eV, which matches the EA of most OSCs, so the ET from D· to OSCs is possible. At 298.15 K, the ΔGs of C-H bond homolysis and heterolysis are +68.3 kcal/mol ~ +71.6 kcal/mol and +62.4 kcal/mol ~ +71.3 kcal/mol, respectively (see Table S2), indicating that both cannot occur at the RT. At 373.15 K, which is the annealing temperature commonly used in the experiments, the ΔGs of C-H bond homolysis and heterolysis are slightly decreased to +66.1 kcal/mol ~ +69.3 kcal/mol and +60.9 kcal/mol ~ +69.6 kcal/mol, respectively, which are still too high for the direct bond dissociation to occur. The ΔG of C-H bond heterolysis is sensitive to the solvent environment due to the stabilizing effect of polar media on charges, and it usually decreases as the permittivity of the solvent increases. Nevertheless, since the permittivity of organic solvents and OSCs (when the reaction occurs in the thin films) are generally small, this effect should be negligible.

The ΔG_{HAT} and ΔG_{HYT} between N-DMBI-H deviates and all the OSCs at 298.15 K are shown in Fig. 2. Remarkably, the ΔG_{HYT} always lies below the ΔG_{HAT}, and all the ΔG_{HAT}s are positive. This is in line with the results of Marder and coworkers. The influence of temperature on ΔGs is negligible: Compared with 298.15 K, the ΔG_{HAT}(373.15 K) is decreased by only ca. 0.4 kcal/mol, and the ΔG_{HYT}(373.15 K) is slightly increased by ca. 0.5 kcal/mol (see Table S3 in Supporting Information). The results demonstrate that thermodynamically, the HYT is more favorable than the HAT. It can be explained by combining Eq. (7) and (8): For a given OSC, if the optimal addition sites of hydrogen atom and hydride are the same, and neglecting the entropy change, Eq. (7) – Eq. (8) gives ΔG_{HAT} – ΔG_{HYT} ≈ EA(AH) – IE(D·), which is always positive because of the small IE(D·); If the addition sites of hydrogen atom and hydride are different, it gives ΔG_{HAT} – ΔG_{HYT} ≈ EA(AH) – IE(D‘) + ΔBDE, where ΔBDE is the difference between the bond dissociation energies (BDEs) of the A-H bond when the hydrogen atom is adsorbed onto the optimal hydrogen-addition site and the optimal hydride-addition site. As shown in Fig. S3 in Supporting Information, the magnitude of
$\Delta$BDE is usually less than 10 kcal/mol, which is much smaller than the $\text{EA}(\text{AH}') - \text{IE}(\text{D}')$ term for most OSCs. As a result, $\Delta G_{\text{HYT}} < \Delta G_{\text{HAT}}$ is satisfied for most of n-type OSCs and N-DMBI-H derivates. The positive $\Delta G_{\text{HAT}}$s can be attributed to the smaller BDE of the A-H bond in most OSCs than that of the active C-H bond in N-DMBI-H derivates. The BDE of the A-H bond is determined by the optimal adsorption sites of H' (H−). The active sites for the nucleophilic attack (H−) can be predicted by the positive Fukui function,57 which is close to the LUMO electron density on atoms. For most OSCs, the optimal adsorption sites of H' and H− are located on the atom that has a large LUMO population (see Figs. S3 and S5 in Supporting Information), they are usually the diimide-oxygens or the carbon atoms connecting different moieties. But this is not valid in some cases, such as TTDPP and BTI where the steric hindrance effect should be considered. Although the optimal adsorption sites might be different, the variation of BDEs between OSCs is usually less than 20 kcal/mol, which is much smaller than the variation of EAs between OSCs (~ 50 kcal/mol). Consequently, for a given dopant, $\Delta G_{\text{HYT}} \propto -\text{EA}(\text{AH}') - \text{BDE}(\text{A-H})$ is governed by the EA of AH', which is proportional to the EA of OSCs. As expected, a roughly linear correlation between the $\Delta G_{\text{HYT}}$ and the EA of OSCs with $R^2 = 0.70$ is observed in Fig. 2. In contrast, the $\Delta G_{\text{HAT}}$, which mainly depends on the BDEs, shows a weak correlation with the EA of OSCs. Similar results are also found for reactions between OSCs and other N-DMBI-H derivates with different C-H homolysis and heterolysis energies, as shown in Fig. 2. The linear correlation between $\Delta G_{\text{HYT}}$ and EA suggests that for OSCs with stronger electron-accepting ability, the HYT is more favorable energetically and the dominance of the HYT against the HAT is more prominent.
3.2 Kinetics of Hydrogen Atom Transfer and Hydride Transfer Reactions

In the above, we have shown that HYT is more favorable than HAT due to its lower \( \Delta G \). To further prove this, we study the kinetics of the bimolecular reactions and calculate the Gibbs free energy of activation, \( \Delta G^\ddagger \). The \( \Delta G^\ddagger \) of HAT or HYT from N-DMBI-H to OSCs are calculated by optimizing the structure of transition states where the trans- 

![Fig. 2](image)

**Fig. 2** The \( \Delta G \)s of HAT and HYT at 298.15 K between N-DMBI-H derivates and OSCs as a function of the EA of OSCs.

...
0.25e transferred from N-DMBI-H (IE = 5.1 eV) to OSCs. But there is a notable $Q_{ET}$ around 0.5e for 2CN-BDOPV and Q-DCM-DPPTT with relatively large EAs (4.3 eV and 4.7 eV, respectively). On the product side, the $Q_{ET}$ can be estimated by the charge on [D] ($Q_D$), $Q_D \approx +1e$ indicates that an integrated electron has been transferred from DH to A, accompanying the [H] transfer, for all the OSCs. Notably, the charge on the [H] species ($Q_H$) is much less than +1e and remains constant during the reaction for all cases except for NDI-T2. In NDI-T2, $Q_H$ increases from +0.25e on the reactant side to +0.5e on the product side, which can be attributed to the electronegativity difference between the donor carbon atom and the acceptor oxygen atom which is the optimal [H]-addition site of NDI-T2. This shows that the transferring [H] species is $H^-$ rather than $H^+$ or proton. All these results strongly support the HYT mechanism that describes the transfer of one hydrogen atom and one electron, and the electron transfer starts with the hydrogen atom transfer. As the $r_{D-H}$ increases, $H^-$ moves from D to A and the amount of electron transfer increases, which is consistent with the HYT via concerted electron and hydrogen atom transfer.

To depict the HYT process, the localized molecular orbitals (LMOs) analysis of N-DMBI-H/2CN-BDOPV in its TS is illustrated in Fig. 3c. We divide the activated complex DHA$^+$ into DH$^+$ and A$^+$, and analyze the interactions between them with LMOs. When the C-H bond is elongated and the bonding orbital of the dopant (labeled as $\sigma_{DH^+}^{(C-H)}$) approaches the empty $\pi^*$ orbital of the OSC that mainly contributed by the $p_z$ orbital on the hydride adsorption atom (labeled as $\pi_{A^+}^* (p_z)$), they interact to form two three-center $\sigma$-type bonds named as $\sigma_{DHA^+}$ and $\sigma_{DHA^+}^*$. The bonding $\sigma_{DHA^+}$ is filled and the antibonding $\sigma_{DHA^+}^*$ has a node on the transferring $H^-$, which is the character of HAT,$^{59, 60}$ and is unoccupied. Meanwhile, as the C-H bond of the dopant is stretched, the energy of $\pi_{DH^+}$ also increases (the upper limit is $E_{SOMO(D)}$), and the $\pi-\pi$ overlap near the reaction center can assist the ET from $\pi_{DH^+}$ to $\pi_{A^+}^*$ at the same time of HAT. Clearly, the larger EA (the smaller IE) of A (D$^-$) will promote the ET to enhance the Coulomb interaction and lower the activation energy, and eventually facilitate the HYT.
The result of LMOs analysis is in line with the Distortion/Interaction energy analysis\textsuperscript{61} (see Figs. S6-7 in Supporting Information). As a result, the $\Delta G^\ddagger$s of 2CN-BDOPV and Q-DCM-DPPTT with larger EAs are significantly smaller than NDI-T2 and C60. It should be noted that there exist several $\pi_{DH}^\ddagger$s and $\pi_A^\ddagger$s that contribute to the ET in the LMOs basis, for brevity, Fig. 3c only shows those with the largest contribution.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) Molecular structures of representative OSCs with EAs, $\Delta G$s, and $\Delta G^\ddagger$s. The optimal [H]-addition sites are highlighted in red. (b) Charges on the [D] and [A] species (Q_D and Q_A), as well as on the transferring [H] (Q_H) along the IRC (plotted as the C-H bond length of the dopant, $r_{D-H}$). (c) Schematic diagrams of the concerted ET and HAT mechanism based on the LMOs of dopant (DH\textsuperscript{2}), OSC (A\textsuperscript{2}, 2CN-BDOPV is chosen as an example), and the activated complex (DHA\textsuperscript{2}) in the TS.}
\end{figure}

Remarkably, the calculated $\Delta G^\ddagger$s and KIE $k_H/k_D$s match well with the experimental results, as shown in Table 1. Combing with the discussions above, these results not only demonstrate the reliability of the calculations but also strongly support that HYT is the real RDS of the doping reaction. The priority of HYT over HAT can be attributed to the moderate hydrogen-donating ability of N-DMBI-H derivate and the moderate electron-accepting ability of OSCs, for which neither the HAT nor the ET is
favored energetically, but the two processes can concert to act as the HYT eventually.

### Table 1. Calculated EA, $\Delta G^\ddagger$, and $k_H/k_D$ and reported experimental results of the doping reactions between N-DMBI-H and several OSCs.

<table>
<thead>
<tr>
<th>OSC</th>
<th>EA(calc.)</th>
<th>$\Delta G^\ddagger$(calc.) (kcal/mol)</th>
<th>$\Delta G^\ddagger$(expt.) (kcal/mol)</th>
<th>$k_H/k_D$(calc.)</th>
<th>$k_H/k_D$(expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM</td>
<td>3.8</td>
<td>20.2</td>
<td>20.4$^b$</td>
<td>3.9</td>
<td>8.6$^b$</td>
</tr>
<tr>
<td>2CN-BDOPV</td>
<td>4.3</td>
<td>7.8</td>
<td>13.9$^c$</td>
<td>4.7</td>
<td>5.1$^c$</td>
</tr>
<tr>
<td>NDI</td>
<td>3.7</td>
<td>21.0</td>
<td>&gt; 22.7$^{cd}$</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>2CN-NDI</td>
<td>3.9</td>
<td>17.5</td>
<td>17.7$^{c}$</td>
<td>5.1</td>
<td>5.8$^c$</td>
</tr>
<tr>
<td>(CN-NDI)$_2$</td>
<td>4.1</td>
<td>20.0</td>
<td>19.4$^c$</td>
<td>4.9</td>
<td>5.3$^c$</td>
</tr>
<tr>
<td>PDI</td>
<td>3.8</td>
<td>22.5</td>
<td>&gt; 22.7$^{cd}$</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>2Br-PDI</td>
<td>3.9</td>
<td>23.7</td>
<td>&gt; 22.7$^{cd}$</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>2CN-PDI</td>
<td>4.3</td>
<td>13.8</td>
<td>19.1$^c$</td>
<td>4.6</td>
<td>5.1$^c$</td>
</tr>
</tbody>
</table>

$^a$ Calculations are based on C60 because there are too many possible hydride addition sites for PCBM.
$^b$ Measured by Ref. 41 in chlorobenzene solution at 300 K.
$^c$ Measured by Ref. 45 in CH$_2$Cl$_2$ solution at 298 K.
$^d$ Estimated according to the rate constant $k < 0.01$ M$^{-1}$ min$^{-1}$.

### 3.3 Molecular Descriptor and Criterion towards High Doping Efficiency

We have demonstrated that the HYT should be the dominant RDS of the doping reaction between N-DMBI-H derivates and a variety of OSCs. In the following, we further discuss the descriptor and criterion for the efficient n-doping and explore the strategies of molecular design to reach high doping efficiency. The $\Delta G^\ddagger$s of HYT between N-DMBI-H and more OSCs are shown in Fig. 4a and Table S4 in Supporting Information. Although the position and elemental type (carbon or oxygen, see Fig. S3) of the hydride-addition sites are different among OSCs, there is a clear Brønsted-Evans-Polanyi (BEP) relation$^{62-64}$ between $\Delta G^\ddagger$ and $\Delta G_{HYT}$ with $R^2 = 0.88$. At 298.15 K, the linear fitting gives

$$\Delta G^\ddagger = 0.52\Delta G_{HYT} + 18.2,$$

(12)

where the slope $\alpha = 0.52$ is close to the 0.54 ~ 0.61 that was measured for the HYT reaction between N-DMBI-H derivates and carbocations reported by Lee et al.$^{65}$ The $\Delta G^\ddagger$ at 298.15 K as a function of the EA of OSCs is shown in Fig. 4b. The $\Delta G^\ddagger$ at 373.15 K is about 4 kcal/mol higher than that at 298.15 K, see Fig. S8 in Supporting
As expected, the $\Delta G^\ddagger$ is correlated linearly to the EA of OSCs, as the $\Delta G_{\text{HYT}}$. The reason is that large EAs can promote the ET from the dopant to OSCs in the activated complex, which in turn enhances the Coulomb attraction and lowers the $\Delta G^\ddagger$. Assuming the doping ratio to be 1:1, the half-time ($t_{1/2}$) of the second-order HYT reaction can be estimated by $t_{1/2} = \frac{1}{[\text{DH}]_0/c^0}$, where $[\text{DH}]_0/c^0 = 0.5$ is the initial concentration, and the rate constant $k$ can be obtained with Eq. (10). For convenience, here the transmission coefficient $\kappa$ in Eq. (10) is set to 1. In experiments, the annealing time for doping processes is on the order of hours, hence, $t_{1/2} < 1$ hour is necessary for efficient n-doping. When $t_{1/2} = 1$ hour is presumed, the $\Delta G^\ddagger$s at 298.15 K and 373.15 K are estimated to be ca. 22 kcal/mol and 28 kcal/mol, respectively. Using the linear relations between $\Delta G^\ddagger$ and EA, the minimum EAs that are required for efficient n-doping (i.e., $t_{1/2} < 1$ hour) at 298.15 K and 373.15 K are ca. 3.5 eV and 3.3 eV, respectively, as indicated in Fig. 4b and Fig. S8.

We now return to the $\Delta G_{\text{HYT}} \propto \text{IE}(D') + \text{BDE}(D-H)$ for a given OSC, and recognize that $\Delta G^\ddagger$ should also correlate to the IE of D·s. Fig. 4c presents the $\Delta G_{\text{HYT}}$ between N-DMB-H derivatives and C60 as a function of the IE of D·s. Clearly, as the IE of D·s increases, the $\Delta G_{\text{HYT}}$ also increases linearly. This is because the BDEs of D-H to form D· and H· are close in these molecules (see Table S1 in Supporting Information), so the $\Delta G_{\text{HYT}}$ is mainly influenced by the electron-donating ability of D·. Recently, Fabiano and coworkers showed that the electrical conductivities and ESR signals of P(NDI2OD-T2) (a polymeric OSC that is simplified as PNDI-T2 in the present work by replacing the alkoxy side-chains with methyl groups) doped by N-DMBI-H and derivatives are positively correlated to the $E_{\text{SOMO}}$ of the dopant radicals.\textsuperscript{44} It can be well explained by Fig. 4c and the HYT mechanism because $E_{\text{SOMO}}$ is proportional to the IE of D· according to the Koopman’s theorem.

The linear correlation between $\Delta G_{\text{HYT}}$ and the EA of OSCs (IE of D·s) roots from a fact that the contribution of the electron-accepting (electron-donating) ability of OSCs (D·s) to the $\Delta G_{\text{HYT}}$ is more significant than the BDE of A-H (D-H). Therefore, we can
take the EA of OSCs and IE of D·s as two molecular descriptors of the reactivity between OSCs and D-H type dopants. It also urges us to further explore the relationship between $\Delta G_{\text{HYT}}$ and the electron transfer driving force, $\Delta = \text{EA(OSC)} - \text{IE(D·)}$. As shown in Fig. 4d, there is a clear linear relation ($R^2 = 0.71$) between $\Delta G_{\text{HYT}}$ and $\Delta$, with $\Delta G_{\text{HYT}}$ decreasing as $\Delta$ increases, which shows the critical role of the electron transfer driving force in the doping process. Because the $\Delta G_{\text{HYT}}$ changes negligibly with temperature, the relation at 373.15 K is analogous to that at 298.15 K, as shown in Fig. S8 in Supporting Information. More importantly, if $\Delta G_{\text{HYT}} \approx 0$ is assumed, it will give $\Delta \approx 1.0$ eV. Hence, $\Delta > 1.0$ eV can be taken as the criterion of $\Delta G_{\text{HYT}} < 0$, which is the thermodynamic criterion for the HYT reaction to occur spontaneously. For example, when N-DMBI-H (IE(N-DMBI·) = 2.8 eV) is the dopant, EA(OSC) > 3.8 eV is required to fulfill the criterion of $\Delta G_{\text{HYT}} < 0$. This is concordant with the outcome of Fig. 2, where the linear fitting of $\Delta G_{\text{HYT}}$ with the EA of OSCs reaches zero at EA(OSC) $\approx 3.8$ eV. This thermodynamic criterion is also stricter than the EA(OSC) > 3.5 eV and EA(OSC) > 3.3 eV kinetic criteria for $t_{1/2} < 1$ hour at 298.15 K and 373.15 K, respectively. Therefore, we propose $\Delta > 1.0$ eV as a robust criterion for the efficient n-doping of OSCs with N-DMBI-H derivates. It is more stringent and reasonable than the $E_{\text{LUMO}}(\text{OSC}) < E_{\text{SOMO}}(\text{D·})$ which is often used to speculate the doping efficiency of OSCs with N-DMBI-H.$^{56, 67}$
Fig. 4 (a) The BEP relation between $\Delta G_{\text{HYT}}$ and $\Delta G^\dagger$. (b) The $\Delta G^\dagger$ of HYT between N-DMBI-H and OSCs as a function of the EA of OSCs. (c) The $\Delta G_{\text{HYT}}$ between different N-DMBI-H derivates and C60, the structures of N-DMBI-H derivates are shown in Fig. S1 in the Supporting Information. (d) $\Delta G_{\text{HYT}}$ as a function of EA(OSC) - IE(D·$^-$). $\Delta = \text{EA(OSC)} - \text{IE(D·$^-$)}$ is the driving force of HYT. (e) The $\Delta G_{\text{HYT}}$ between N-NDMBI-H and OSCs as a function of the EA of OSCs which are highlighted as per the backbone structures, see Fig. S4 in the Supporting Information. (f) The $\Delta G_{\text{HYT}}$ between N-DMBI-H and reported as well as designed polymers as a function of the EA of OSCs. (g) The chemical structures of LPPV and four designed polymers with the torsion angle about the double-bond linkage labeled. (h) Bond length distortion between anion and neutral states of the oligomers indicating the polaron delocalization along the chain. The calculations are based on oligomers with a similar backbone length (~ 6 nm): Pentamer for LPPV, hexamer for BzBI, and tetramer for TITI.

3.4. Molecular Design of N-Type Organic Semiconductors

Discovery of these exciting relationships between the EA (IE) of OSCs (D·$^-$), $\Delta G_{\text{HYT}}$, and $\Delta G^\dagger$ is truly important to the molecular design of OSCs to achieve high n-doping efficiency. According to the $\Delta = \text{EA(OSC)} - \text{IE(D·$^-$)} > 1.0$ eV criterion, the n-doping efficiency can be improved by enhancing the EA of OSCs or reducing the IE of D·$^-$s. However, there have been quite few OSCs reported showing large EAs. Designing
OSC s with large EAs is not only important for the high n-doping efficiency, but also for the stable electrical conduction in the air. Usually, it can be achieved by chemical substitutions with electron-withdrawing groups.\textsuperscript{68, 69} Here, we provide an alternative route to design conducting polymers with large EAs and good planarity simultaneously. Noticeably, most of the polymers with large EAs and favorable $\Delta G_{\text{HYT}}$ have double-bond linkages between aromatic moieties, i.e., the quinoid-like backbone structures, such as TBDPPV, BDPPV, and LPPV (see Fig. 4e and Fig. S4 in Supporting Information). Hence, tuning the heteroatom fused-ring structures linked by the double-bond is an effective strategy to design conducting polymers with large EAs. Several quinoid-like small-molecule and polymeric OSCs with high EAs have been successfully synthesized.\textsuperscript{70, 71} As presented in Fig. 4g, four quinoid-structure polymers, named as TIBI, BzBI, TIBF, and TITI, are designed based on the structure of LPPV, a quinoid-like polymer whose EA was measured to be 4.5 eV by the cyclic voltammetry (CV) method,\textsuperscript{72} and calculated to be 4.4 eV (Fig. 4f). The designed polymers could be synthesized through metal-free aldol-catalyzed polymerization.\textsuperscript{71, 72} Actually, an excellent conducting polymer with the backbone structure similar to LPPV, large EA, and ultra-high $\sigma$ exceeding 2000 S/cm was reported very recently.\textsuperscript{11} Our calculations confirm that all these designed polymers exhibit $\text{EA} > 4.0$ eV, and $\Delta G_{\text{HYT}} < 0$ when doped with N-DMBI-H. These values are comparable to those of the best performing polymers already reported (Fig. 4f). Besides, the backbone planarity of these designed polymers is much better than LPPV, owing to the small steric hindrance between neighboring moieties (see the torsion angle around the double-bond linkage shown in Fig. 4g). As a result of the better backbone planarity, the polarons in BzBI, TIBF, TIBI, and TITI are found to be more delocalized than in LPPV, as manifested by the structural distortion in the polymer anions and its distribution along the chain (Fig. 4h and Fig. S9 in Supporting Information). These results support that the designed polymers with large EAs are potential n-type OSCs that may be effectively doped by N-DMBI-H and may show excellent charge transport property.

Last but not least, it should be noted that the extremely large EA of OSCs may also cause the rapid doping reaction at RT before the formation of thin films, which could
be detrimental to the film morphology and deteriorate charge transport because Coulomb attraction between the ionized dopants and OSCs in solution might disrupt the packing of OSCs.\textsuperscript{34,73} Therefore, a rational design and match of n-dopants and OSCs to control the thermodynamics and kinetics of HYT based on the findings in this work will substantially accelerate the development of n-type OSCs towards high doping efficiency and high electrical conductivity.

4. Conclusions

In summary, we study the HAT and HYT reactions between N-DMBI-H derivates and commonly available OSCs in the process of n-doping. We compare the free energy changes of the two reactions $\Delta G_{\text{HAT}}$ and $\Delta G_{\text{HYT}}$, and confirm that the HYT is more favorable than the HAT thermodynamically. After analyzing the electronic structure, the charge transfer, and bonding characteristics of the activated complex, and comparing the calculated $\Delta G^\dagger$s and KIEs with experiments, we conclude that the HYT, or more specifically, the concerted electron and hydrogen atom transfer, is the real RDS of the n-doping process. In the meanwhile, we discover two important linear relations between the $\Delta G_{\text{HYT}}$ and the EA (IE) of OSCs (dopant radicals D$^-$), based on which we propose two molecular descriptors of the reactivity between N-DMBI-H type dopants and OSCs, namely, the EA of OSCs and the IE of dopant radicals, D$^-$. More strikingly, the $\Delta G_{\text{HYT}}$ is found to be negatively correlated to the electron transfer driving force, defined as $\Delta = \text{EA(OSC)} - \text{IE(D$^-$)}$, and according to the second law of thermodynamics that requires $\Delta G_{\text{HYT}} < 0$, a $\Delta > 1.0$ eV criterion for high doping efficiency is suggested to replace the widely accepted $E_{\text{LUMO(OSC)}} < E_{\text{SOMO(D$^-$)}}$. The molecular descriptors are facile molecular properties, the new criterion is more stringent, and easy to apply in the high-throughput screening of n-type OSCs and dopants. As a demonstration, quinoid-like polymers with EA > 4.0 eV and good backbone planarity are designed as potential n-type OSCs. The findings in this work have tremendously deepened our understandings of the doping mechanism of n-type OSCs, and provided straightforward guidelines for the molecular design of both OSCs and n-dopants to achieve improved doping efficiency and conductivity.
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Supporting Information

Molecular structures of all dopants and OSCs; Optimal hydrogen atom and hydride adsorption sites on OSCs; EAs of OSCs; IEs of dopants and dopant radicals; Thermodynamic parameters of HAT and HYT at 298.15 K and 373.15 K; Kinetic parameters of HYT at 298.15 K and 373.15 K.

Conflict of interest

The authors declare no competing interest.

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