The splitting of quasi-Fermi levels (QFLs) represents a key concept utilized to describe finite-bias operations of semiconductor devices, but its atom-scale characterization remains a significant challenge. Herein, the nonequilibrium QFL or electrochemical potential profiles within single-molecule junctions obtained from the first-principles multispace constrained-search density-functional formalism are presented. Benchmarking the standard nonequilibrium Green’s function calculation results, it is first established that algorithmically the notion of separate electrode-originated nonequilibrium QFLs should be maintained within the channel region during self-consistent finite-bias electronic structure calculations. For the insulating hexanethiolate junction, the QFL profiles exhibit discontinuities at the left and right electrode interfaces and across the molecule the accompanying electrostatic potential drops linearly and Landauer residual-resistivity dipoles are uniformly distributed. For the conducting hexatrienedithiolate junction, on the other hand, the electrode QFLs penetrate into the channel region and produce split QFLs. With the highest occupied molecular orbital entering the bias window and becoming a good transport channel, the split QFLs are accompanied by the nonlinear electrostatic potential drop and asymmetric Landauer residual-resistivity dipole formation. Our findings underscore the importance of the first-principles extraction of QFLs in nanoscale junctions and point to a future direction for the computational design of next-generation semiconductor devices.

**Significance**

A universal feature of semiconductor devices is that the functional channel region is driven out of equilibrium, or formally it cannot be characterized by one global Fermi level. Naturally, the concept of quasi-Fermi (imref) levels (QFLs) and their splitting was introduced, and it has now become a standard theoretical tool to describe finite-bias nonequilibrium operations of semiconductor devices. However, after 70 years from its inception by Shockley, the first-principles calculation of QFLs still remains to be achieved. Applying a recently developed ab initio approach, we herein calculate the QFLs in molecular junctions and particularly for a conducting single-molecule junction establish the correlations among the splitting of QFLs, nonlinear electrostatic potential drop, and asymmetric Landauer residual-resistivity dipole distribution.

**Author contributions:** Y.-H.K. designed research; J.L., H.Y., and Y.-H.K. performed research; J.L. and Y.-H.K. contributed new reagents/analytic tools; J.L., H.Y., and Y.-H.K. analyzed data; and J.L. and Y.-H.K. wrote the paper.

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electrochemical potentials is accompanied by an asymmetric nonlinear electrostatic potential drop across the molecule. We thus clarify the nontrivial correlations between the electrochemical and electrostatic potential drop profiles at the atomic scale.

**Results and Discussion**

**Electron Occupation Rule for Nonequilibrium Channel States.** While the electrochemical potentials or QFLs are in principle defined as the occupation of nonequilibrium energy levels, it is in practice a nontrivial matter to compute them in a first-principles manner. It should be noted that in the standard DFT-NEGF formalism (6, 7), the explicit determination of QFLs is avoided as follows: First, DFT-NEGF invokes the Landauer picture in the formalism (6, 7), the explicit determination of QFLs is avoided. As the occupation of nonequilibrium energy levels, it is in practice a nontrivial matter to compute them in a first-principles procedure based on certain approximations on the formal definition. Within the MS-DFT formalism, we now adopt finite-sized L and R electrodes (microcanonical ensembles) and explicitly extract the Kohn–Sham (KS) states by performing the multipurpose constrained-search procedure or total-energy minimizations with the constraint of $eV_b = \mu_L - \mu_R$. A key step is then, during the self-consistent construction of nonequilibrium charge densities, variationally occupying the channel KS states with a proper occupation rule or determining the channel electrochemical potential $\mu_C$. In establishing the occupation rule, a reasonable approach would be to assume that the eigenstates of the L-C-R system can be divided into one group originating from L and right-traveling with a population function $f_L$, and the other group originating from R and left-traveling with a population function $f_R$. Note that this more or less corresponds to the scheme that was implicitly used in the implementation of DFT-NEGF in the form of Eq. 1. Additionally, as implied also in the approximation of Eq. 1 within DFT-NEGF, we will assume the situation when there does not exist within the bias window any state that is strictly localized in the C region. To embody the rule within MS-DFT, we thus for each C state (i.e., the state with the biggest weight in region C) assessed the L and R weights and filled the level according to (Fig. 1 B, Top and see SI Appendix for the formal definition)

Occupation rule I: $f_C(E - \mu_C) \rightarrow \begin{cases} f(E - \mu_L) & \text{L-originated:} \\ f(E - \mu_R) & \text{R-originated:} \end{cases}$

Rather than dealing with multiple split QFLs explicitly, one might also want to consider only a single averaged electrochemical potential. So, we additionally tested the equal-weight averaging occupation rule (Fig. 1 B, Bottom).

Occupation rule II: $f_C(E - \mu_C) \rightarrow f(E - \mu_L + \mu_R)/2$,

which could be a representative scheme of generating the local electrochemical potential that was found to be useful for postprocessing analysis (11, 12, 17).

**Fig. 1.** The occupation rule of nonequilibrium channel states within the MS-DFT formalism. (A) Schematic of the QFL distribution and charge-transport processes in a nanoscale device. According to the Landauer picture, one considers a channel (C) sandwiched between the left (L) and right (R) electrodes. Upon applying a positive voltage $V_L$ to $R$, the electrochemical potentials of $L$ and $R$ shift to $\mu_L$ and $\mu_R = \mu_L - eV_b$, respectively. The imbalance between right/left-moving electrons (arrows) will drive C into a nonequilibrium state and the nature of $\mu_C$ will determine charge-transport characteristics. (B) Schematics of the occupation rules for the (C) states tested within MS-DFT. Depending on the spatial distribution of each KS wave function, we assigned either separate $\mu_L$ and $\mu_R$ (rule I) or averaged ($\mu_L + \mu_R)/2$ (rule II). (C) The optimized structure of the HDT junction model. Red, green, and blue boxes indicate the L, C, R regions, respectively, within the MS-DFT or DFT-NEGF calculations. (D) The plane-averaged electrostatic potential difference $\Delta\varphi$ calculated within DFT-NEGF (black dashed line) and MS-DFT with the occupation rule I (red solid lines) or rule II (blue solid lines) for the HDT junction at $V_b = 1.0$ V (Top) and the HTD junction at $V_b = 0.6$ V (Bottom). The red, green, and blue down triangles, respectively, indicate the locations of the L-, C-, and R-region interface Au layers marked in C.
Carrying out the MS-DFT calculations for the single-molecule junction models based on the HDT and HTDT molecules and benchmarking the DFT-NEGF calculation results, we now heuristically determine the validity of the above two occupation rules. In modeling the junctions (Fig. 1C), we considered the S-Au linkages based on a single-apex Au atom or coordination number 1 S-Au contacts, for which the molecular states are energetically pulled up as close as possible to the equilibrium Fermi level $E_F$ (18). In carrying out the self-consistent DFT-NEGF and MS-DFT calculations, we applied the Fermi function with a temperature of 300 K to both $L$ and $R$ reservoirs. Here, we comment that we view the finite temperature $T$ in the electrode regions as an independent degree of freedom and its introduction can be justified within the Mermin’s finite-temperature DFT formulation (19). In Fig. 1D, we show for the HDT and HTDT junctions under $V_b = 1.0$ and 0.6 V, respectively, the plane-averaged bias-induced electrostatic potential change profile,
\[
\Delta \mathbf{V}_H(\mathbf{r}) = \mathbf{V}_{H}^\mu(\mathbf{r}) - \mathbf{V}_{H}^\nu(\mathbf{r}),
\]
where $\mathbf{V}_{H}^\mu$ and $\mathbf{V}_{H}^\nu$ are the classical Hartree Coulomb potentials at the nonequilibrium and equilibrium conditions, respectively. The corresponding exchange-correlation potential variations are much smaller and will not be explicitly discussed below (SI Appendix, Fig. S1). It can be then immediately found that, for both the HDT and HTDT junction cases, the DFT-NEGF $\Delta \mathbf{V}_H$ curves (black dotted lines) are accurately reproduced by the MS-DFT $\Delta \mathbf{V}_H$ ones only within the occupation rule I that explicitly maintains two separate $\mu_L$ and $\mu_R$ (red solid lines). On the other hand, with the averaging occupation rule II, we obtain the MS-DFT $\Delta \mathbf{V}_H$ (blue solid lines) that significantly deviates from the DFT-NEGF $\Delta \mathbf{V}_H$. It should be commented here that, for the HTDT junction case, the adaptation of the coordination number 3 S-Au contact or shifting the HOMO further away from $E_F$ and out of the bias window (18) enabled the DFT-NEGF $\Delta \mathbf{V}_H$ to be reproduced by MS-DFT within both the occupation rules I and II (SI Appendix, Fig. S2). As will be discussed shortly, the HTDT junction behaves as a simple tunneling barrier, and the HOMO originates from the spatially localized S states. We thus conclude that the average occupation approach II is appropriate only for insulating junctions with simple electrode–channel interfacial electronic structures. We consider that these findings are in line with the earlier claim on the validity of the local electrochemical potential concept only in the linear-response regime or low-temperature and low-bias conditions (17). Having confirmed that algorithmically it is essential to maintain the notion of two separate $\mu_L$ and $\mu_R$ during self-consistent nonequilibrium electronic structure calculations, we will below present only the MS-DFT calculation results obtained with the occupation rule I.

**Nonequilibrium Quantum Transport Characteristics.** We now examine in detail the quantum transport properties of the two molecular junctions. In Fig. 2A and B, we first present the current–bias voltage ($I-V_b$) characteristics of HDT and HTDT junctions, respectively, which show the insulating character of the former and the conducting character of the latter. While alkane–dihiolate molecular junctions have been extensively investigated both experimentally and theoretically (14, 15), studies on polyene–dithiolate counterparts are scarce (16, 20) despite the important roles played by polyenes for bioprocesses such as vision and photosynthesis (21). Due to the conjugated nature of HTDT or the presence of three double bonds, the HTDT junction produces currents about two orders of magnitude larger than those from its HDT counterpart.

To understand this large discrepancy between their current-carrying capacities, we observe the transmission functions and the corresponding molecule-projected density of states (DOS) obtained at $V_b = 0.6$ V. The very different $I-V_b$ characteristics are the direct results of negligible transmissions in the HDT junction within the bias window (Fig. 2C, Left) and the single near-unity transmission peak right below the middle of the bias window ($\mu_L + \mu_R)/2$ in the HTDT case (Fig. 2D, Left). However, the projected DOS data show that the HDT HOMO enters the bias window (Fig. 2C, Right, left filled triangle) as its HTDT counterpart (Fig. 2D, Right, left filled triangle).

These seemingly contradictory results can be understood in terms of the spatial distributions of the two HOMOs, and for this purpose, we present in Fig. 2E and F the molecular-projected Hamiltonian (MPH) analysis (22) data and in Fig. 3A and B the spatially resolved DOS. The local DOS of the HDT junction (Fig. 3A) then show that the equilibrium HDT HOMOs are

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**Fig. 2.** Quantum transport properties of the HDT and HTDT junctions calculated within MS-DFT and DFT-NEGF. Current–bias voltage ($I-V_b$) curves of the (A) HDT and (B) HTDT junctions. Black dashed lines with cross marks and red unfilled circles indicate the results obtained from the DFT-NEGF and MS-DFT calculations, respectively. Insets display the corresponding chemical structures of the molecules. Transmission spectra (Left) and projected DOS (Right) of the (C) HDT and (D) HTDT junctions at $V_b = 0.6$ V. Black dashed lines and red solid lines represent the data obtained from the DFT-NEGF and MS-DFT calculations, respectively. In each case, black left triangle indicates the HOMO level. (C, Inset) Transmission curve in the logarithmic scale. Three-dimensional contour plots of the molecular-projected Hamiltonian HOMO derived from the (E) HDT and (F) HTDT junctions. In E and F, the isosurface level is 0.01 Å$^{-3}$. 

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initially composed of two states localized at the left and right S sites, and at finite \( V_b \), due to their disconnected nature, the left and right interfacial states are independently pulled up and down, respectively. The localized character of the left S-based HOMO, which corresponds to the DOS peak within the bias window in Fig. 2 C, Right (indicated by the left triangle), can be also clearly observed in the visualized MPH-state visualization shown in Fig. 2 E.

Similarly, we can establish the correlation between the spatial distribution of the HTDT HOMO and the conducting nature of the HTDT junction: The most notable feature from the MPH visualization shown in Fig. 2 F and the local DOS plot shown in Fig. 3 B is the highly delocalized nature of the HTDT HOMO-originated state (left triangle in Fig. 2 D, Right). Due to this delocalization, in contrast to the splitting of the HOMO into two decoupled states in the HDT case (Figs. 2 C and 3 A), the equilibrium HOMO maintains its identity even at finite \( V_b \) (a single DOS peak in Fig. 2 D, Right; see also Fig. 3 B) and produces a near-unity transmission peak for the HTDT junction (Fig. 2 D, Left).

**Equivalence and Comparison of DFT-NEGF and MS-DFT.** At this point, we emphasize that, as shown throughout in Fig. 2, the \( I-V_b \), transmission, DOS, and MPH visualization data obtained based on MS-DFT are in excellent agreement with the DFT-NEGF data in both the insulating HDT and conducting HTDT junction cases (SI Appendix, Fig. S2). While we previously reported the accordance between DFT-NEGF and MS-DFT calculation results for van der Waals heterostructures (13), the demonstration of such correspondence here for covalently bonded molecular junctions reinforces the validity of adopting the MS-DFT formalism to describe nonequilibrium quantum transport processes.

Before presenting the electrochemical potentials uniquely available in MS-DFT, we further discuss several computational outputs that can be commonly obtained from the DFT-NEGF and MS-DFT calculations. First, we point out that the MPH eigenstates shown in Fig. 2 E and F were obtained by diagonalizing a nonequilibrium Hamiltonian matrix derived from a cluster system, namely by introducing an arbitrarily defined supercell that contains a vacuum and with a Γ-point sampling, as a postprocessing step. We will present below the KS states obtained from self-consistent MS-DFT calculations, which more clearly exhibit the bulk crystal wave-function characteristics in the electrode regions.

Next, we consider the bias-induced electrostatic potential changes and the corresponding charge-density differences. Comparing the \( \Delta \rho_H \) profiles of the HDT and HTDT junctions shown as black solid lines in Fig. 3 A and B as well as Fig. 1 D, we note that, while it drops uniformly across the molecule in the former (Fig. 1 D, Top and Fig. 3 A), \( \Delta \rho_H \) drops more abruptly on the left electrode–molecular interface in the latter (Fig. 1 D, Bottom and Fig. 3 B). The sharp electrostatic potential drop at the left S site for the HTDT junction case is more noticeable in the contour plot representations shown in the bottom panels of Fig. 3 C and D for the HTDT and HTDT junctions at \( V_b = 0.6 \) V, respectively. To understand their implications, we additionally analyzed the bias-induced charge-density difference,

\[
\Delta \rho(\vec{r}) = \rho^I(\vec{r}) - \rho^0(\vec{r}),
\]

where \( \rho^I \) and \( \rho^0 \) are the charge densities of each junction at the nonequilibrium and equilibrium conditions, respectively. The contour plots of \( \Delta \rho \) of the HDT and HTDT junctions at \( V_b = 0.6 \) V are shown in the top panels of Fig. 3 C and D, respectively, and we find that \( \Delta \rho \) is rather uniformly distributed across the molecule in the HTDT junction case but is concentrated near the left S site in the HTDT counterpart. Corresponding to the Landauer residual-resistivity dipole (23, 24), they then translate into the linear voltage drop across the channel in the HDT junction and the abrupt voltage drop at the left electrode–channel contact in the HTDT junction. Here, it should be
reminded that, in addition to the electrostatic potential $\Delta V_{1,2}$ drop, the question of where the “voltage drop” can be also addressed in terms of the electrochemical potential $\mu$ drop (17, 24). Their spatial variations can deviate from each other within the nonequilibrium nanoscale channel region, and the discrepancies between electrostatic and electrochemical potential drops will become clearer in the subsequent discussions of the QFLs that are uniquely available within the MS-DFT approach.

**First-Principles Determination of QFLs.** While we established the correlations between electrostatic potential drops and Landauer residual-resistivity dipole distributions at finite-bias voltages, the microscopic origin of the formation of a strong resistivity dipole on the left $S$ site in the HTDT junction case remains unclear. We now demonstrate that the consideration of QFL profiles, or the delocalized $\text{QFL states}$, we observe both states localized at the Au surface absent within the molecular backbone region. Analyzing the $\text{MS-DFT}$ formalism. In selecting the KS states to be visualized, we color-coded electron occupation factors obtained within the MS-projection KS wave functions together with the corresponding $\text{MS-DFT}$ weights in the $\text{xy}$-$\text{plane}$-formed nature of the QFLs. $\text{MS-DFT}$–derived QFL profiles of the HDT and HTDT junctions under $V_b = 0.6$ V in Fig. 4 $A$ and $B$, respectively. Here, we chose to represent the QFL profiles in terms of the $\text{xy}$-plane-projected KS wave functions together with the correspondingly color-coded electron occupation factors obtained within the $\text{MS-DFT}$ formalism. In selecting the KS states to be visualized, we extracted the $\Gamma$-point states with the electron occupancy values between 0.001 and 0.999.

If we first consider the HTDT junction case (Fig. 4 $A$), the simple tunneling barrier nature of HDT (negligible transmissions within the bias window in Fig. 2 $C$, Left), QFLs are absent within the molecular backbone region. Analyzing the QFL states, we observe both states localized at the Au surface regions (indicated by gray arrows) and those delocalized through the Au region and connected to the $S$ states (for the details, see $\text{SI Appendix}$, Fig. S3). We find that, while the former localized states support the linear electrostatic potential drop (black solid line), the latter states propagate from the deep $L$ and $R$ Au regions into the left and right $S$ sites at $\mu_L$ (marked as $\circlearrowright$) and $\mu_R$ (marked as $\circlearrowleft$), respectively. Visualization of the $\circlearrowright$ and $\circlearrowleft$ states in Fig. 4$C$ more intuitively reveals the spatially discontinuous nature of the QFLs.

Moving to the HTDT junction QFL profiles (Fig. 4$B$), we find that much richer and significantly different features emerge. Within the Au electrode regions, compared with the HDT junction case, more left (right) electrode states near the $\mu_L$ ($\mu_R$) energy range participate in forming QFLs. More importantly, within the channel region, we observe that the QFLs split into the HTDT HOMO (marked as $\circlearrowright$ in Fig. 4$B$) as well as the left- and right-electrode-originated states ($\circlearrowright$ and $\circlearrowleft$ in Fig. 4$B$, respectively; for the details, see $\text{SI Appendix}$, Fig. S4). While the QFL splitting was introduced in the early development of $\text{semiconductor device physics}$ for the basic concepts such as the $p-n$ junction (1), electron–hole recombination (2), and solar cell (3), to our knowledge, its first-principle determination has not been reported yet.

Based on the spatial distributions of the three states $\circlearrowright$, $\circlearrowleft$, and $\circlearrowright$ and $\circlearrowleft$ and their energetic locations (Fig. 4 $B$ and $D$), we finally explain the atomistic origins of the near-unity transmission peak (Fig. 2 $D$, $\text{Left}$) and the nonlinear electrostatic potential drop in the HTDT junction (solid black line in Fig. 4$B$). First, we can see that the delocalization of the HTDT HOMO $\circlearrowright$ into both the right and left Au electrode regions results in an almost perfect transmission (Fig. 4 $D$, $\text{Middle}$). In addition, because the HTDT HOMO energetically lies more closely to $\mu_R$, we observe that the coupling of the HTDT HOMO with the $R$ states becomes much stronger than that with the $L$ states. Note that this also implies that even if a wave function has significant and almost equal weights in the $L$ and $R$ regions in equilibrium, the symmetry is automatically broken in the nonequilibrium state (for the details, see $\text{SI Appendix}$, Fig. S5). Accordingly, despite the symmetric junction geometry, there arises a stronger (weaker) $\text{pileup}$ of electrons or resistivity-dipole formation on the left (right) electrode–molecule interface, which in turn causes more abrupt electrostatic potential drop at the left contact. In view of its importance in semiconductor device applications (1–3), we can

![Fig. 4.](image-url)
suggest that the nontrivial correlations between the finite-bias voltage drop and the splitting of the QFLs would be a promising target for measurements with atomic-scale spatial resolution. This might be achieved by, e.g., combining the scanning tunneling potentiometry (8–10) and multiprobe scanning tunneling spectroscopy techniques (25).

Conclusions

In summary, we calculated the nonequilibrium QFLs across the nanoscale junctions based on saturated HDT and conjugated HTDT molecules. The first-principles extraction of QFLs was enabled by the recently developed MS-DFT approach, the key features of which are partitioning the Kohn–Sham states into the left-electrode/channel/right-electrode regions and variationally determining the occupations of channel states with a finite-bias constraint. Benchmarking the standard DFT-NEGF calculation results, we first established that during self-consistent nonequilibrium electronic structure calculations it is necessary to adopt an occupation rule that maintains the notion of nonlocal or two separate electrode-originated QFLs within the channel region. For the insulating HDT junction case, we observed the QFLs that are spatially discontinuous at the left and right molecule–electrode interfaces, which translate into a linear electrostatic potential drop and Landauer residual-resistivity dipoles uniformly distributed across the molecular channel. On the other hand, for the conducting HTDT junction counterpart, we observed that the channel-region QFLs split into multiple states originating from the two electrodes and the molecule. Moreover, with the HTDT HOMO entering into the bias window as a good transport channel, we observed the development of a nonlinear electrostatic potential drop and correspondingly the asymmetric residual-resistivity dipole distributions despite the symmetric junction geometry. Clarifying the nontrivial correlations among the QFL splitting, electrostatic potential drop, and Landauer residual-resistivity dipole formation in nonequilibrium channel regions, our findings underscore the importance of the first-principles extraction of QFLs in nanoscale junctions and point to a future direction for the technology computer-aided design of advanced electronic, optoelectronic, and electrochemical devices.

Materials and Methods

DFT Calculations. Based on our earlier works (18, 20, 26), we modeled the HTD- and HTDT-based single-molecule junctions by adopting the trans configuration for both molecules and introducing one apex Au atom on top of the 4 × 4 Au(100) slabs. The gap distance between Au electrodes was set to 23.7 Å in terms of the atomic positions of the first Au layers within the L and R reservoir-region electrodes (red and blue down arrows in Fig. 1C, respectively). We carried out equilibrium DFT calculations using the SIESTA software (27) within the local density approximation (28). Double-ζ-plus-polarization-level numerical atomic orbital basis sets were employed together with the Troullier–Martins-type norm-conserving pseudopotentials (29). The mesh cutoff of 200 Ry for the real-space integration, and 2×2×1 Monkhorst-Pack k-points grid sampling of the Brillouin zone were used. The C-region atomic geometries were optimized until the total residual forces on each atom were below 0.02 eV/Å.

DFT-NEGF and MS-DFT Calculations. For the finite-bias nonequilibrium electronic structure calculations, we used the DFT-NEGF method implemented within the TraniSIESTA code (30) and our in-house MS-DFT method implemented within the SIESTA code (13). A key feature of MS-DFT that distinguishes it from DFT-NEGF is that the introduction of the self-energy Σ = ggsRΣz, where ggs is the surface Green’s function and Σz is the electrode–channel coupling matrix, is not performed within the self-consistent electronic structure calculations but postponed until the post-self-consistent quantum transport calculations. Remaining within the microcanonical picture, we invoke the transport-to-optical excitation mapping viewpoint and utilize the space-resolved constrained-search procedure with the constraint of evR = μL − μR. Then, based on the variational (time-independent) DFT formulations for electronic excitations established by Göring (31) and Levy–Naggy (32), one can once again adopt an effective DFT formalism

for first-principles nonequilibrium electronic structure calculations. We thus complete the finite-bias electronic structure calculations without introducing Σ and explicitly produce the nonequilibrium KS states together with their occupancies.

Once the converged nonequilibrium electronic structure is obtained for a junction using MS-DFT, we finally recover the Landauer or grand-canonical transmission spectra with respect to the bias voltage U, and the reflection matrices. For the comparison of MS-DFT and DFT-NEGF calculation results, we adopted the same L/CIR partitioning scheme (Fig. 1C) and used identical ggs. The transmission functions were then obtained according to

\[ T(E; V_b) = \frac{1}{G_L(R)} \left[ \sum_{\mu} \Gamma_L(R) \Gamma_R(L) \Gamma_{\mu}^*(L) \Gamma_{\mu}^*(R) \delta(E - \mu) \right], \]

where \( G \) is the retarded Green’s function for the channel C and \( \Gamma_{\mu} = \sum_{\delta} \delta \Gamma_{\mu} \) are the broadening matrices. The numerical convergence of transmission spectra with respect to the k-point sampling in the HTDT junction case is provided in SI Appendix, Fig. S6. The \( \Gamma_{\mu} \) characteristics were calculated by invoking the Landauer–Buttiker formula,

\[ \Gamma_{\mu} = 2 \pi \sum_{\delta} \Gamma_{\mu} \delta(E - \mu) - (E - \mu) \delta(E - \nu) \]

The MPH analyses on DFT-NEGF and MS-DFT calculation output were performed using the Inelastic code (22).

Data Availability Statement. All relevant data are provided in the main text and/or SI Appendix.

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