Semimetallicity and Negative Differential Resistance from Hybrid Halide Perovskite Nanowires

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In the rapidly progressing field of organometal halide perovskites, the dimensional reduction can open up new opportunities for device applications. Herein, taking the recently synthesized trimethylsulphonium lead triiodide \((\text{CH}_3)_3\text{SPbI}_3\) perovskite as a representative example, first-principles calculations are carried out and the nanostructuring and device application of halide perovskite nanowires are studied. It is found that the 1D \((\text{CH}_3)_3\text{SPbI}_3\) structure is structurally stable, and the electronic structures of higher-dimensional forms are robustly determined at the 1D level. Remarkably, due to the face-sharing \([\text{PbI}_6]\) octahedral atomic structure, the organic ligand-removed 1D PbI\(_3\) frameworks are also found to be stable. Moreover, the PbI\(_3\) columns avoid the Peierls distortion and assume a semimetallic character, contradicting the conventional assumption of semiconducting metal-halogen inorganic frameworks. Adopting the bundled nanowire junctions consisting of \((\text{CH}_3)_3\text{SPbI}_3\) channels with sub-5 nm dimensions sandwiched between PbI\(_3\) electrodes, high current densities and large room-temperature negative differential resistance (NDR) are finally obtained. It will be emphasized that the NDR originates from the combination of the near-Ohmic character of PbI\(_3\)-(\text{CH}_3)_3\text{SPbI}_3 contacts and a novel NDR mechanism that involves the quantum-mechanical hybridization between channel and electrode states. This work demonstrates the great potential of low-dimensional hybrid perovskites toward advanced electronic devices beyond actively pursued photonic applications.

1. Introduction

Organic–inorganic hybrid halide perovskites have recently emerged as prominent candidates for optoelectronic applications due to their high light absorption coefficient, long charge carrier diffusion length, intense photoluminescence, slow nonradiative charge recombination rate, and defect tolerant nature.\(^1\)\(^{-8}\) Together with their low cost and facile fabrication process, these excellent material properties allowed hybrid perovskites to show enormous potential in optoelectronic device applications such as solar cells, light-emitting diodes, lasers, and photodetectors.

Particularly, as a method to achieve novel material properties and optimized device performance, organic–inorganic hybrid perovskites have been recently made into atomically thin 2D sheets and 1D nanowire structures.\(^9\)\(^{-11}\) These low-dimensional halide perovskites with strong quantum confinement and spatial isolation effects have demonstrated great promise for the tuning of photoluminescence peaks and the improvement of device performances.\(^12\)\(^{,13}\) In fact, low-dimensional 2D and 1D forms of halide perovskites were an active research target about two decades ago\(^14\)\(^{-16}\) and are recently regaining interest in view of their optoelectronic device applications. Overall, compared with their photonic counterparts, research on the electronic devices based on both 3D and low-dimensional hybrid halide perovskites has been scarce.

In this work, we explore the novel material and device properties of low-dimensional hybrid halide perovskites in view of realizing advanced electronic devices, and predict the emergence of semimetallic behavior from the inorganic framework of 1D halide perovskites and from their heterojunctions excellent negative differential resistance (NDR) characteristics. As a specific case, we consider recently synthesized trimethylsulfonium lead triiodide perovskite, \((\text{CH}_3)_3\text{SPbI}_3\) (TMSPbI\(_3\)), which showed an 1D-based crystal structure and good ambient stability.\(^17\)\(^{,18}\) In terms of the atomic structure, TMSPbI\(_3\) consists of hexagonal stacks of 1D columns made of face-sharing \([\text{PbI}_6]\) octahedra, and individual anionic 1D PbI\(_3^-\) columns are surrounded and isolated by the organic \((\text{CH}_3)_3\text{S}^+\) (TMS\(^+\)) cations. Despite the hint of possibly deriving isolated 2D and 1D nanostructures from the parental TMSPbI\(_3\), so far the structural, electronic, optical properties of 1D TMSPbI\(_3\) and its 2D network have not been considered yet.

Carrying out density functional theory (DFT) calculations, we confirm that 2D monolayer and 1D nanowire structures derived from 3D TMSPbI\(_3\) are dynamically stable, and the electronic structures of 3D and 2D TMSPbI\(_3\) analogs are essentially determined by that of the 1D component. Most intriguingly, it is found that the inorganic 1D PbI\(_3\) framework remains structurally stable even after organic ligands are stripped off, and furthermore it exhibits a semimetallic character. Having structurally stable and yet electronically distinct nanowire components out of the bulk TMSPbI\(_3\), we finally devise bundled...
nanowire heterojunctions in which semiconducting TMSPbI₃ channels with sub-5 nm dimensions are sandwiched between semimetallic PbI₃ electrodes. Carrying out DFT-based nonequilibrium Green's function (NEGF) calculations, we then obtain strong NDR properties characterized by high current density (in the range of ≈900 kA cm⁻²) and peak-to-valley current ratios (PVRs, up to ≈17) at low-bias regimes (<0.5 V). It will be emphasized that the predicted NDR results from the combination of a novel NDR mechanism based on quantum-mechanical hybridization of channel electronic states and the unique near-Ohmic character of PbI₃-TMSPbI₃ contacts.[19]

2. Results and Discussion

2.1. Structure and Stability of TMSPbI₃ and PbI₃ Nanowires

In Figure 1a–c, we show the atomic structures of 3D bulk, 2D nanosheet, and 1D nanowire TMSPbI₃ perovskites, respectively, optimized within the Perdew–Burke–Ernzenhof parameterization of generalized gradient approximation revised for solids (PBEsol).[20] The inorganic PbI₃ nanowire structure prepared by removing trimethylsulfonium (CH₃)₃S⁺ ligands is additionally presented in Figure 1d, and we will later show that it is also a dynamically stable structure. The experimentally synthesized TMSPbI₃ 3D crystal structure has hexagonal symmetry in the space group P6₃mc (no. 186), and what particularly attracted our attention was the presence of an 1D network of inorganic PbI₃ frameworks that are individually composed of face-sharing [PbI₆] octahedra and the absence of amine in organic TMS cations. The 1D chains of distorted face-sharing [PbI₆] octahedra along the c-axis could be the medium for efficient charge transport. In addition, the 1D PbI₃ columns are surrounded by two TMS⁺ ligands per unit cell (UC), which apparently stabilize the face-sharing coordination of [PbI₆] octahedra and, possibly due to the absence of labile protons accompanying protonated amine cations, induce the long-term stability of TMSPbI₃ in air.[17] In the 1D TMSPbI₃ nanowire, due to the removal of steric hindrance imposed by neighboring 1D nanowires, the ligands are rotated and shifted slightly away from the positions in 3D and 2D structures and results in a noticeable symmetry breaking with respect to the axial planes (Figure 1c). On the other hand, after completely removing TMS⁺ ligands, we observe that the 1D PbI₃ column recovers the highly symmetric structure (Figure 1d; see also Figure S1 in the Supporting Information for a detailed analysis of 1D PbI₃ crystal structure).

To explore the feasibility of obtaining isolated 2D and 1D nanostructures from the experimentally synthesized 3D form, we further calculated interlayer and intercolumn binding or exfoliation energies for the former and the latter cases, respectively. We obtained the interlayer binding energy of 17.7 meV atom⁻¹ for the 2D layer and the intercolumn binding energy of 44.8 meV atom⁻¹ for the 1D nanowire. Our calculated interaction strength for 2D and 1D nanostructures lies within the range that permits the mechanical exfoliation to synthesize freestanding nanostructures in experiments (≤150 meV atom⁻¹).[21] These interlayer and intercolumn binding energy values were compared with DFT-D3[22] results, and we confirmed that they remain within the experimentally accessible range for exfoliation (For the details, see Table S1 in the Supporting Information). Because the air-stable nature of the parental TMSPbI₃ results from the utilization of TMS⁺ cations,[17] we expect that the 2D and 1D TMSPbI₃ will be also stable in air.

![Figure 1](image-url)  
**Figure 1.** Crystal structures of low-dimensional TMSPbI₃ analogs and a NDR device model. The atomic geometries in a) 3D bulk, b) 2D monolayer, c) 1D nanowire, and d) 1D PbI₃ inorganic core-only analogs. Distortion or symmetry breaking in the inorganic face-sharing octahedral framework can be noted in the left panel (c). The black dotted boxes in panels (a)–(d) indicate the unit cells for each case. e) The optimized atomic structure of bundled nanowire junctions based on PbI₃ electrodes and TMSPbI₃ channels (green box region). Red and blue (including green) box regions in inset (e) indicate the (semi-infinite) electrodes and central scattering regions, respectively, within NEGF transport calculations.
Finally, in addition to the 2D and 1D nanostructuring, we also considered the feasibility of obtaining stable inorganic PbI$_3$ columns by removing organic ligands from TMSPbI$_3$. Calculating the ligand binding energy with reference to the trimethylsulfonium iodide (CH$_3$)$_3$SI, which was used in experiments as the precursor to synthesize TMSPbI$_3$,[17,18] we obtained $-1.1 \text{ eV \ formula-unit}^{-1}$. While the magnitude is in line with the unique role of the sulfur-based ligands to stabilize the octahedral face-sharing 1D PbI$_3$ frameworks during the synthesis of TMSPbI$_3$, it is comparable to the widely exploited gold-thiolate surface binding energies.[23–25] So, we expect that it will be possible to selectively remove TMS$^+$ ligands from TMSPbI$_3$ through chemical cleaning processes such as the controlled ozone treatment.[26]

Having confirmed the feasibility of preparing isolated 2D sheet and 1D nanowire TMSPbI$_3$ forms, we further explored their dynamic stabilities by calculating their phonon spectra (Figure 2; see Figure S2 in the Supporting Information for the 3D case). We find that imaginary phonon modes are absent in the phonon band dispersion curves, which confirms the dynamical stability of 2D and 1D nanostructures. Regarding the role of TMS$^+$ ligands, we observe that unstable phonon modes emerge when one of the two ligands in the 1D UC is removed (Figure S3, Supporting Information) and conclude that the isometric distribution of ligands around the inorganic 1D PbI$_3$ column is required to structurally stabilize TMSPbI$_3$. Most interestingly, however, if all the TMS$^+$ ligands are removed, the inorganic 1D PbI$_3$ framework becomes again a dynamically stable structure as shown in Figure 2c. The mechanisms of the structural stabilization of PbI$_3$ will be discussed below together with the analysis of its electronic structure.

2.2. Electronic and Optical Properties of TMSPbI$_3$ Nanowires

In Figure 3a,b, we respectively show the calculated electronic band structures and optical absorption spectra of 2D and 1D TMSPbI$_3$ perovskites as well as the ligand-removed 1D PbI$_3$ (see also Figure S4 in the Supporting Information for the bulk TMSPbI$_3$ data). Here, to correct the well-known bandgap underestimation within the local and semilocal DFT exchange–correlation functionals, we employed the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional.[27] In addition, due to the presence of heavy Pb atoms, we included spin–orbit coupling (SOC) effects, which resulted in the splitting of conduction band bottom energy bands and the resulting reduction of bandgaps compared to the non-SOC values (see Table S2 and Figure S5 in the Supporting Information for the detailed comparisons between the results obtained without and with SOC). Then, for the bulk TMSPbI$_3$ case, we obtained the bandgap of 3.25 eV, which is in good agreement with the experimentally measured optical bandgap of 3.15 eV.[17,18] Experimentally, this bandgap value was extracted by assuming an excitonic absorption, or excluding the peak right above the absorption onset, and our calculation of optical spectra that neglects local field effects provides the direct confirmation of the assumption (see Figure S4b in the Supporting Information). The subband gap excitonic peak in the measured optical spectra is rather prominent.[17,18] While we do not attempt to reproduce this excitonic absorption peak by resorting to the many-body approach or time-dependent DFT formalism,[28,29] it clearly indicates the large quantum confinement effect even in the bulk limit or the electronically decoupled nature of individual 1D TMSPbI$_3$ columns.

The comparison of 1D and 2D TMSPbI$_3$ band structures (Figure 3a and Table 1) and optical spectra (Figure 3b) with those of their 3D counterpart (Figure S4, Supporting Information) show the detailed nature of quantum confinement effects. Specifically, we find that the electronic structures of the 3D and 2D TMSPbI$_3$ are essentially identical to that of the 1D analog. The intrinsically 1D nature of TMSPbI$_3$ as well as the above-presented stability of its low-dimensional forms can be understood in terms of the
connected face-sharing octahedral structure of the PbI\textsubscript{3} framework and the absence of physical sharing between these 1D PbI\textsubscript{3} columns. The calculated electronic band structures of the TMSPbI\textsubscript{3}-derived 3D and 2D structures indicate that they are slightly indirect band gap semiconductors, and that the difference between indirect and direct gaps is reduced with the reduction in dimensionality, leading to the direct band gap of 3.33 eV in the 1D TMSPbI\textsubscript{3} case. Analyzing the projected density of states (DOS) shown in Figure 3a (see also Figure S4a in the Supporting Information), we find that band edges in bulk and low-dimensional analogs are mainly contributed by the core inorganic region PbI\textsubscript{3}, whereas the electronic states related to the organic ligands (CH\textsubscript{3})\textsubscript{3}S\textsuperscript{+} are located at the energy ranges away from band edges. The dissemination of integrated charge density around band edge regions in the 1D case further shows that the valence band maximum (VBM) primarily originates from I 5p orbitals, while the conduction band minimum (CBM) is produced from Pb 6p and I 5p orbitals (Figure 3c; see Figure S6 in the Supporting Information for more detailed exposition of VBM and CBM electronic wavefunctions at different Brillouin zone points and Figure S7 in the Supporting Information for the orbital contributions to the DOS of these band edges). Unlike in the 3D and 2D counterparts, we find that the CBM of 1D case is partly contributed by (CH\textsubscript{3})\textsubscript{3}S\textsuperscript{+} ligand states. We note that this feature is unique to the 1D case, and is in line with the above-discussed distortion of inorganic core framework (Figure 1c) that results in the stronger hybridization between organic ligand and inorganic core states. The calculated optical absorption peaks in 3D (Figure S4b, Supporting Information) and 2D structures (Figure 3b) exhibit relatively stronger intensity along the octahedral face-sharing TMSPbI\textsubscript{3} column axial direction (ε\textsubscript{2}) than along the weakly connected normal direction (ε\textsubscript{1}), and particularly the former is in good agreement with the experimental spectrum shape.

### 2.3. Semimetallicity from PbI\textsubscript{3} Inorganic Frameworks

We now consider the inorganic 1D PbI\textsubscript{3} case, which was earlier found to be dynamically stable even after (CH\textsubscript{3})\textsubscript{3}S\textsuperscript{+} ligands are removed. Strikingly, we find that it exhibits semimetallic characteristics with a linear dispersion at the Fermi level (E\textsubscript{F}), which implies that the Peierls distortion is absent in 1D PbI\textsubscript{3}. To confirm the stability of the semimetallicity in 1D PbI\textsubscript{3}, we stretched and compressed the inorganic octahedral framework along the c-axis and observed that the semimetallicity is robustly preserved (Figure S8, Supporting Information). On the other hand, considering the 1D PbBr\textsubscript{3} column derived from (CH\textsubscript{3})\textsubscript{3}SPbBr\textsubscript{3}, which has been also synthesized recently,\textsuperscript{18} we find that the structure becomes dynamically unstable and goes through a Peierls distortion (Figure S9, Supporting Information). To further analyze the origin of the absence and presence of Peierls distortion in the inorganic PbI\textsubscript{3} and PbBr\textsubscript{3} columns, respectively, we analyzed the local DOS of PbI\textsubscript{3}, PbBr\textsubscript{3} and symmetry-enforced (unstable) PbBr\textsubscript{3} structures. The comparison shows that, while the 1S lone-pair orbitals spatially interact with each other in the PbI\textsubscript{3} case, such neighbor interactions do not exist for the Br 4p lone-pair orbitals in the symmetry-enforced 1D PbBr\textsubscript{3} counterpart. Namely, due to the large atomic size of I, the circumferential I–I interactions will prevent the distortion of

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**Figure 3.** Electronic and optical properties low-dimensional forms of TMSPbI\textsubscript{3}. a) Electronic band structures and projected DOS of 2D and 1D semiconducting TMSPbI\textsubscript{3}, and 1D semimetallic PbI\textsubscript{3} calculated within HSE. The top of occupied bands is set to zero in 2D and 1D TMSPbI\textsubscript{3} cases. For the band structures, we also show the PBEsol results. In the DOS plots, we show the projections to Pb, I, and (CH\textsubscript{3})\textsubscript{3}S. b) The imaginary parts of the complex dielectric functions of 2D TMSPbI\textsubscript{3}, 1D TMSPbI\textsubscript{3}, and 1D PbI\textsubscript{3} calculated within HSE. Blue and red curves in the 2D TMSPbI\textsubscript{3} case are the optical spectra along the TMSPbI\textsubscript{3} column axial (ε\textsubscript{2}) and normal (ε\textsubscript{1}) directions. c) Integrated charge densities around the band edges of 1D TMSPbI\textsubscript{3} and PbI\textsubscript{3}. While VBM and CBM band edge states are shown for 1D TMSPbI\textsubscript{3}, two VBM peak states are shown for 1D PbI\textsubscript{3} indicated as ① and ②. The isosurface level is 3 x 10\textsuperscript{-3} e Å\textsuperscript{-3}.
[PbI₆] octahedral cages in the PbI₃ case or suppress the Peierls distortion. Apparently, with the smaller atomic size of Br, the PbBr₃ counterpart lacks such a mechanism and undergoes a Peierls distortion or distortions of the [PbBr₆] octahedral cages. This could become a useful guideline for the future research on low-dimensional halide perovskite inorganic frameworks.

Finally, in terms of the optical spectra presented in Figure 3b, we note that PbI₃ exhibits a plasmonic absorption peak at around 1.6 eV. This nanowire plasmon character suggests the potential of metallic 1D PbI₃ for novel applications that were not previously considered for hybrid halide perovskite materials alone. For example, the incorporation of plasmonic nanoparticles in a perovskite film was previously shown to improve the photovoltaic efficiency and our finding implies that such an effect might be achieved with the interfaces purely based on hybrid perovskite-derived materials. While such studies appear promising, we now introduce a completely new research direction for hybrid halide perovskites, that is, the negative differential resistance effect.

2.4. Ultrahigh NDR Characteristics from Halide Perovskite Nanowire Junctions

Given the presence of novel semiconducting TMSPbI₃ and semimetallic 1D-PbI₃ nanowires, we carried out DFT-based NEGF calculations and studied the bias-dependent quantum transport processes in bundled nanowire junctions. The transport device model was derived directly from the 3D TMSPbI₃ and is composed of semiconducting TMSPbI₃ channels sandwiched by metallic PbI₃ electrodes as shown in Figure 1e (see Figure S10 in the Supporting Information for the details). The current density–bias voltage (J–Vₖ) characteristics obtained for the three to five UC (3UC–5UC) TMSPbI₃ channels are shown in Figure 4a. We observe that, as summarized in Table 1, excellent NDR performances characterized by very high peak current density (reaching ≈4750 kA cm⁻² for the 3UC case) and PVRs as large as a few tens (reaching ≈17.4 for the 5UC case) are achieved with sub-5 nm long channels in low-bias voltage regimes (<0.5 V). Moreover, these excellent NDR characteristics were obtained at room temperature, and they were robustly preserved down to the zero temperature limit (see Figure S11 in the Supporting Information).

To understand the mechanisms behind the strong NDR signals, we first show in Figure 4b the zero-bias Eₕ transmission eigenstates propagating from the left PbI₃ electrode. We observe an overall very strong penetration of metallic PbI₃ states into the semiconducting TMSPbI₃ channel region, which indicates that our device operates based on quantum tunneling. The penetration length of PbI₃ states is over two UC length, which explains the exceptionally high current density level as well as rapid initial increase of currents in the 3UC channel case.

Next, to explain the bias voltage Vₖ dependence of tunneling currents, we show in Figure 4c the development of transmission spectra for the 5UC case with the increasing Vₖ (see Figure S12 in the Supporting Information where the transmission spectra for the 3UC, 4UC, and 5UC cases are compared). In Figure 4d, we also show the corresponding molecular projected Hamiltonian (MPH) eigenstates that contribute most strongly to the transmissions. The isosurface level is 5 × 10⁻⁴ e Å⁻³.

Figure 4. The NDR device properties from TMSPbI₃ perovskite nanowires. a) The J–Vₖ characteristics of the 4UC and 5UC channel junctions. b) Left transmission eigenchannels at Vₖ = 0.0 V. c) Transmission spectra for 5UC device at different Vₖ values. Grey shaded regions indicate the bias windows. Note that Vₖ = 0.25 and 0.46 V correspond to the NDR peak and NDR valley regions, respectively. d) Molecular projected Hamiltonian states for the 5UC case at different Vₖ values that contribute most strongly to the transmissions. The isosurface level is 5 × 10⁻⁴ e Å⁻³.
quantum tunneling. We note that until $V_b = 0.25$ V (the NDR peak point) the MPH eigenstates (~0.091 and ~0.043 eV for the $V_b = 0.15$ and 0.25 V cases, respectively) are strongly delocalized through the channel region. As long as the delocalized MPH eigenstates or large transmission functions are maintained, the widening of bias window will result in current enhancements. However, upon further increasing the bias voltage to $V_b = 0.46$ V (the NDR valley point), we observe that the spatial connectivity of MPH eigenstates with the right terminal region is abruptly broken, indicating the suppression of transmissions or reduction of currents.

### 2.5. The Quantum-Hybridization NDR Mechanism

We finally analyze the nonlinear $J–V_b$ characteristics in more detail and show that it is a manifestation of a novel NDR mechanism. In Figure 5a–d, we present the development of projected local DOS across a PbI$_3$-5UC TMSnPbI$_3$-PbI$_3$ junction with increasing $V_b$. Remind that in the resonant tunneling diode and tunnel diode, which have the largest parallel with our device in that the device characteristics have quantum mechanical origins, the NDR signals arises from the (intraband) tunneling across two barriers in the former case (Figure 5e) and the band-to-band (interband) tunneling in the latter (Figure 5f). However, our perovskite nanowire junctions involve neither two barriers nor the band-to-band tunneling. Instead, the NDR signal in our case is produced by the quantum-mechanical hybridization between left and right electrode states in the low-bias regime ($V_b = 0.15$ V and 0.25 V) and its abrupt disruption in the high-bias regime ($V_b = 0.46$ V). Note the strong presence of (two) electrode Fermi-level states penetrating into the channel at finite bias,[36] which are symmetrically tilted until $V_b = 0.3$ V and then abruptly broken into an asymmetric form at $V_b = 0.46$ V. Although much smoothened out compared with electrochemical potentials,[36] electrostatic potentials also show a corresponding transition from the symmetric low-bias ($V_b \leq 0.3$ V) to asymmetric high-bias ($V_b \geq 0.3$ V) profiles.

### Table 1. NDR characteristics of devices based on 3UC, 4UC, and 5UC channel models.

| Model | Channel length [nm] | Peak voltage [V] | Valley voltage [V] | Peak current density [kA cm$^{-2}$] | Valley current density [kA cm$^{-2}$] | PVR |
|-------|---------------------|------------------|-------------------|------------------------------------|------------------------------------|-----|
| 3UC   | 2.4                 | 0.32             | 0.49              | 4753.8                             | 1058.5                             | 4.5 |
| 4UC   | 3.2                 | 0.28             | 0.47              | 1195.1                             | 73.5                               | 16.3|
| 5UC   | 4.0                 | 0.25             | 0.46              | 920.7                              | 52.8                               | 17.4|

Figure 5. The “quantum-hybridization NDR” mechanism. Projected local DOS and energy band diagrams of the 4UC model at a) $V_b = 0.0$ V, b) $V_b = 0.15$ V, c) $V_b = 0.25$ V, and d) $V_b = 0.46$ V. The CBM-region data are not shown for clarity. The solid and dotted lines indicate the Fermi levels in the PbI$_3$ electrodes and the quasi-Fermi levels in the TMSnPbI$_3$ channel, respectively. For comparison, the band alignments at the NDR peak regimes in e) the resonant tunneling diode based on the double-barrier tunneling and f) the tunnel diode based on the band-to-band tunneling are schematically depicted.
(Figure S13, Supporting Information). While we recently showed[37] that this “quantum-hybridization NDR” mechanism is also the origin of the NDR signals recently observed in 2D van der Waals heterostructure transistors,[18–40] the perovskite nanowires with a negligible Schottky barrier or near-Ohmic contacts[19] at the PbI3-TMSPbI3 interfaces apparently produce higher current densities and NDR PVRs.

3. Conclusions
In summary, taking the recently synthesized TMSPbI3 hybrid halide perovskite as a representative example, we carried out first-principles calculations to investigate the material properties and electronic device applications of halide perovskite nanowires. The energetic and dynamical stabilities of low-dimensional TMSPbI3 forms were confirmed by computing exfoliation energies and phonon band dispersions, respectively. In the process of nanostructuring from the 3D bulk to the 1D nanowire limits, these structures showed very small variations in their electronic and optical spectra, revealing their intrinsically 1D nature. Notably, we predicted that the inorganic framework of TMSPbI3 consisting of distorted face-sharing [PbI6] octahedra is also structurally stable and moreover assumes a semimetallic property, inviting the experimental realization of the novel PbI3 form. Given the possibility of deriving metallic as well as semiconductor nanowire elements from the parent TMSPbI3 perovskite structure, we finally considered the PbI3-TMSPbI3-PbI3 nanowire junction models and obtained very strong NDR characteristics. We emphasized that the results provide a proof of concept for the novel “quantum-hybridization NDR” mechanism that involves the quantum-mechanical hybridization of channel electronic states with their electrode counterparts at low bias-voltages and its abrupt disruption at higher bias voltages. Our work demonstrates the significant potential of low-dimensional hybrid halide perovskites for post-CMOS electronic devices that will enable, e.g., low-power multivalued logic applications,[39,40] encouraging the research community to move beyond the photonic applications for which halide perovskites have been mainly considered.

4. Experimental Section
DFT Calculations: The PBEsol[20] and HSE[27] DFT calculations were performed with the Vienna Ab-initio Simulation Package.[41] The plane-waves were expanded with a kinetic energy cutoff of 600 eV to obtain basis sets with the self-consistency cycle convergence energy criterion of 10−4 eV. A k-point mesh of 5 × 5 × 8, 1 × 5 × 8, and 1 × 1 × 8 was employed for 3D, 2D, and 1D structures, respectively. Atomic structures were optimized using conjugate-gradient approach until the Hellmann–Feynman forces were less than 0.001 eV Å−1. The simulations were performed within the PBEsol generalized gradient approximation.[20] The core and valence electrons were handled by the projector augmented wave method.[41] A vacuum space of more than 15 Å was inserted perpendicular to the periodic directions of 2D nanosheet and 1D nanowire perovskites to avoid interactions with their neighboring images in periodic boundary condition setup. In order to determine the dynamic stability of (CH3)3PbI3 nanostructures, we adopted the 2×2×3, 1×3×3, and 1×1×4 supercells for of 3D and 2D, and 1D cases, and computed the force constant matrices by using the small displacement method. In the electronic band structure calculations, we included the SOC and its effects are discussed in Table S2 and Figure S5 in the Supporting Information.

DFT-NEGF Calculations: Quantum transport calculations were performed by using the TranSIESTA software[42] that implements the NEGF method.[36,43] The PBEsol generalized gradient approximation[20] was employed together with the double-ζ plus polarization-quality atomic orbital basis sets. The device geometry was optimized until atomic forces become smaller than 0.04 eV Å−1. The MPH orbitals were generated using the Inelastica code.[14]

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

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Conflict of Interest
The authors declare no conflict of interest.

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