One-dimensional Magnetic MX₃ Single-Chains (M=Cr, V and X=Cl, Br, I)

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Magnetic materials in reduced dimensions are not only excellent platforms for fundamental studies of magnetism, but they play crucial roles in technological advances. The discovery of intrinsic magnetism in monolayer two-dimensional van der Waals systems has sparked enormous interest, but the single-chain limit of one-dimensional magnetic van der Waals materials has been largely unexplored. Here, we report on a family of one-dimensional magnetic van der Waals materials with composition MX₃ (M= Cr, V, and X= Cl, Br, I), prepared in fully-isolated fashion within the protective cores of carbon nanotubes. Atomic-resolution scanning transmission electron microscopy identifies unique structures that differ from the well-known 2D honeycomb lattice MX₃ structure. Density functional theory (DFT) calculations reveal charge-driven reversible magnetic phase transitions.

1. INTRODUCTION

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Magnetism at surfaces, interfaces, and in low-dimensional materials generally has long been of central interest for both fundamental research and technological advances^[1]. The reduced dimensionality often leads to strong spin fluctuations that affect magnetic ordering and give rise to a variety of novel magnetic phenomena^[2] including enhanced magnetic anisotropy. These characteristics underpin device applications such as magnetic storage, spintronics, and magnetic sensing^[1a, 1g]. Recent discoveries of intrinsic magnetism in two-dimensional (2D) van der Waals materials have intensified the search for new atomically thin magnetic materials, and single 2D layers of $CrI_3^{[1e]}$, $Cr_2Ge_2Te_6^{[1e]}$, $FePS_3^{[3]}$, $VSe_2^{[4]}$, and $MnSe_2^{[5]}$ are prime examples. However, there has been limited exploration of other dimensional polymorphs, particularly one-dimensional (1D) chain structures. Moreover, although some quasi-1D magnetic materials have received modest attention, the synthesis of fully isolated, truly 1D single chain magnets has proven difficult. In a promising recent advancement^[6], some single $CrCI_3$ chains were observed amongst collections of multi-chain $CrCI_3$ bundles grown on NbSe₂ substrates. Synthesis and further experimental studies of such structures are exceedingly challenging because of the sensitivity of halide materials to light, oxygen, and moisture^[7].

One promising method for fabricating and enabling further characterization of sensitive 1D structures is to employ hollow-core nanotubes as nano-reaction vessels. Carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) have facilitated synthesis of various materials, including monoelements^[8], metal halides^[9], chalcogenides^[10], and perovskites^[11]. The geometrical-confinement effect imposed by the cavities inside the nanotube can lead to the formation of crystal structures and morphologies that are unknown in bulk counterparts^[10d, 10e, 10g, 10k]. A small inner diameter nanotube can favor 1D structures, as it constrains the radial dimension for the encapsulated material^[9b, 10k]. The use of nanotube sheaths provides protection against oxidation and enables experimental study of 1D nanostructures that are not air-stable^[9b, 10g]. Furthermore, especially in the case of CNT encapsulation, possible charge transfer between the CNT and the core chain provides an additional control parameter for altering material properties.

Here, we report the creation and study of a family of one-dimensional (1D) magnetic van der Waals single-chains of MX₃ (M= Cr, V and X= Cl, Br, I), fully isolated within the cores of CNTs. Nanotube encapsulation enables stabilization the structure of the 1D MX₃ single-chains, and simultaneously prevents environmental degradation, facilitating detailed structural characterization. Atomic-resolution scanning transmission electron microscopy (STEM) imaging and simulation clearly identify the 1D MX₃ chain configurations. The 1D MX₃ chains consist of face-sharing MX₆ octahedra, in distinct contrast to the edge-sharing octahedral found in the complementary 2D honeycomb lattice MX₃ structure. Density functional theory (DFT) calculations reveal that a significant fraction of electronic charges is transferred from the CNTs to the chain. The electron transfer stabilizes the face-sharing single-chain structure against the edge-sharing layered structure, and strongly affects the magnetic energies of the chains. Notably, CrX₃ chains tend to undergo antiferromagnetic (AFM) to ferromagnetic (FM) transitions as a function of electron doping.

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CrI₃ chains are directly synthesized by vacuum annealing CrI₃ precursors in the presence of open-ended nanotubes at high temperatures (see Methods section for the details). The samples are primarily screened using transmission electron microscopy (TEM) to confirm that the target material has successfully filled inside the nanotubes. The atomic structure of the filled-material is further investigated using annular dark field (ADF) aberration-corrected STEM.

Figure 1a shows an atomic-resolution ADF-STEM image of a 1D CrI₃ single-chain encapsulated within a nanotube with an inner diameter of 1.1 nm. The CrI₃ chain encapsulated nanotubes are filled to around 90% with chain length of several hundred nanometers (Supporting Figure S1). The composition ratio of the encapsulated CrI₃ is determined by energy-dispersive spectroscopy (EDS), which confirms a composition 25.4 ± 2.8 atomic percent (atom %) Cr and $74.6 \pm$ 3.6 atom %, yielding an atomic ratio X/M=2.9 (expected ratio = 3). The ADF-STEM image contrast strongly depends on the atomic number (Z) which allows direct distinguishing of Cr (Z_{Cr}=24) from I (Z_I=53). Our DFT binding energy calculations (Supporting Figure S2) show that CrI₃ single-chains are most stable when encapsulated within a nanotube of inner diameter 1.1 nm for both metallic armchair and semiconducting zigzag CNTs; this critical diameter is corroborated by our experimental observations for metallic CNTs.

Based on the observed STEM images, we find that the 1D CrI_3 chain structure consists of face-sharing CrI_6 octahedra along the chain axis (Figure 1b and Supporting Figure S3). Figures 1c and 1d are magnified high-resolution (HR) ADF-STEM images at the different viewing directions (0° and 90°, respectively), which clearly show the atomic structure of 1D CrI_3 . Figures 1e and 1f show intensity line profiles from the regions marked in Figures 1c and 1d, respectively. In the case of a 0° rotated image, the intensity difference of I₂ and I₁ along the chain direction is clearly distinguishable. The uniform intensities of I₁ are obtained from the 90° rotated image. The lattice constant along the chain directions is 6.8 Å from the observed images. The simulated STEM images are generated using

the identified atomic structure, which match well with the experimentally observed results, as shown in Figure 1g and 1h.

The observed face-sharing in 1D CrI₆ octahedrons is different from that observed in the 2D CrI₃ counterpart. While the 2D CrI₃ also contains the same octahedrons, they are connected to each other in an edge-sharing mode to form a 2D honeycomb lattice (Supporting Figure S4). Similar 1D face-sharing octahedral MX₃ chain structures are observed in other quasi-1D crystals such as β -TiCl₃^[12] and β -RuCl₃^[13]. We emphasize, however, that our observed 1D CrI₃ chain structure, and the isolation of this chain in a single-chain form, have not been previously reported. 2D CrI₃ often requires graphene or h-BN encapsulation for protection from ambient exposure or light-induced damages. We find that the synthesized CrI₃ chains inside nanotubes are stable under ambient exposure. The nanotube reaction vessel not only facilitates the formation of interesting structures but also provides an effective barrier against oxidation, as has been noted in prior research^[9b, 10g, 11].

Extending the above findings for CrI₃, we study the 1D MX₃ single-chain with different metal and halogen combinations. In our study we use in-house synthesized crystals of CrBr₃ and VI₃, as well as commercially available powders of CrCl₃, VBr₃, and VCl₃ for MX₃ encapsulated nanotube fabrication (See Methods section for details). **Figure 2** shows the experimental and simulated atomicresolution STEM images of 0°-rotated MX₃ single-chains within the nanotube with different halogens and metals. All synthesized MX₃ single-chains inside the nanotube consist of face-sharing octahedral, identical to the CrI₃ case. The experimentally observed STEM images (left side) of CrBr₃, VI₃, and VBr₃ show similar image contrast to those of CrI₃ (Figures 2a, 2c, and 2d) as here again the atomic numbers of the metals ($Z_V = 23$ and $Z_{cr} = 24$) are lower than those of the corresponding halogens ($Z_I =$ 53 and $Z_{Br} = 35$). In the case of CrCl₃ and VCl₃, the atomic number of Cl ($Z_{cl} = 17$) is lower than that of the metals, resulting in lower intensity compared to the metals (Figures 2b and 2e). The simulated STEM images (right side) of the MX₃ chain also show good agreement with the experimental results. The 90°-rotated simulated STEM images are shown in Supporting Figure S5.

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The measured lattice constants of the MX₃ chains along the chain direction are 6.3 Å for CrBr₃, 6.0 Å for CrCl₃, 6.8 Å for VI₃, 6.3 Å for VBr₃, and 6.0 Å for VCl₃, respectively (Supporting Figure S6). The lattice constant of the MX₃ materials is primarily influenced by the halogen element rather than the transition metal. The size of the halogen ion affects the distance between neighboring atoms, which in turn affects the lattice constant. Transition metals, on the other hand, have a minor influence on the lattice constant of these materials. Our results strongly suggest that the face-sharing 1D MX₃ chain structures inside nanotubes can be stabilized universally in MX₃ compounds.

We now theoretically investigate the atomic, electronic and magnetic properties of MX₃ single-chains by using first-principles DFT calculations. We first focus on isolated MX₃ single-chains with no surrounding nanotube. The atomic positions of isolated MX₃ single-chains are optimized by minimizing the total energy. The optimized lattice parameters are in excellent agreement with the experimental lattice parameters as shown in **Table 1**. For all MX₃ compounds, the MX₆ octahedra are elongated along the chain axis compared to the ideal octahedral structure. Although the elongation brings a small splitting of t_{2g} orbitals into a doubly-degenerate $e^{\pi g}$ and a nondegenerate a_{1g} orbital^[14], three (two) t_{2g} electrons in Cr³⁺ (V³⁺) magnetic ions remain fully spin-polarized to form S=3/2 (S=1) antiferromagnetic (ferromagnetic) chains (**Figures 3**a and 3b). CrCl₃, CrBr₃, and VI₃ have the easy axis perpendicular to the chain axis, and CrI₃, VCl₃, and VBr₃ parallel to the chain axis. For both Cr and V chains, the magnetic anisotropy is the strongest for chains with iodine. We note that the dependence of the magnetic anisotropy on the ligand atom is also pronounced in the monolayer CrX₃, where the spin-orbit coupling of the ligand atom plays the dominant role in determining the magnetic anisotropy energy^[15].

We now determine the magnetic exchange parameters of the one-dimensional anisotropic Heisenberg model $H = \sum_{i < j} J_{ij}^{||} S_j^{||} S_j^{||} + J_{ij}^{\perp} S_i^{\perp} \cdot S_j^{\perp}$, where $S_i^{||}$ and S_i^{\perp} are spin operators parallel and perpendicular to the easy axis, respectively, and $J_{ij}^{||}$ and J_{ij}^{\perp} are corresponding exchange interaction parameters. First, we obtain the density matrix of isolated MX₃ single-chains in vacuum including the spin-orbit interaction, and then the exchange parameters are calculated based on the magnetic force .5214095, ja, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/adma.202307942 by Univ of California Lawrence Berkeley National Lab, Wiley Online Library on [27/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms

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theorem^[16]. Supporting Figure S7 shows the calculated exchange interaction parameters as a function of distance between spins. We find that the magnetism of CrX_3 and VX_3 chains are of localized and itinerant character, respectively. For CrX_3 , the magnetic interactions are short-ranged and XXZ-type $(J_{ij}^{||} \neq 0)$. The dominant exchange parameters for CrX_3 are summarized in Table 1. On the other hand, VX_3 has oscillating and slowly decaying exchange interactions, which indicates itinerant magnetic interactions.

Supporting Figure S8 shows the calculated electronic structures of isolated nanotube-free MX₃ single-chains. Cr-based chains are insulating when in either a ferromagnetic or antiferromagnetic state. Interestingly, the conduction bands of CrX₃ chains in the AFM phase are extremely flat and energetically well isolated. The narrow bandwidth can be understood as arising from kinetic frustration^[17], where the direct hopping between Cr *d* orbitals destructively interfere with indirect hopping mediated by *p* orbitals in the halide atoms (See Supporting Figure S9 showing the conduction band wave functions). A related example is also pointed out in our recent study^[10k]. Since those conduction bands of CrX₃ chains can provide an excellent platform to study correlated electron physics in one dimension^[2b]. On the other hand, ferromagnetic VX₃ chains are half-metals where majority spin states are metallic and minority spin states are insulating with a large band gap over 2 eV.

To illustrate the role of nanotube encapsulation, we examine theoretically MX₃ single-chains encapsulated within CNTs. Figures 3c and 3d show that, because of the work function mismatch, an electronic charge transfers from the CNT. The amount of the electron transfer is around 0.25 e per formula unit (f.u.) and does not sensitively depend on the composition. The additional electrons from the CNT are distributed among both transition metal and halide atoms in the chain. Our previous studies also have pointed out significant charge transfer arises in CNT-encapsulated 1D materials^[10b, 10h, 18]. The charge transfer makes the encapsulating CNTs hole-doped, which can have experimental signatures such as raising of the Raman G band frequency in CNTs^[19]. 15214095, ja, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/adma.202307942 by Univ of California Lawrence Berkeley National Lab, Wiley Online Library on [27/10/2023], See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Ceative Commons

To understand the effects of electron doping to MX₃ chains, we calculate the electron doping dependence of MX₃ single-chains in vacuum. Figure 3e compares the total energies of MX₃ in the single-chain phase against the monolayer phase consisting of a honeycomb structure of edge-sharing octahedra. While the monolayer phase is more stable without electron doping, the single-chain phase quickly becomes more stable with electron doping. When the doping amount is 0.25e/f.u., which represents the amount of the electron transfer from the CNT, all MX₃ chains are more stable than their monolayer counterparts. This shows that electron transfer from the CNT plays a crucial role in further stabilizing the single-chain phases. For single-chain CrCl₃ synthesized on NbSe₂ substrates, charge transfer may similarly aid stabilization of the chain structure^[6]. In addition, our calculations show that the magnetic states of MX₃ single-chains are strongly affected by electron doping. Figure 3f shows the magnetic energy as a function of electron doping. CrX₃ chains are antiferromagnetic at the neutral phase but they become ferromagnetic as electrons are added. Based on the results presented in Figure 3f, the critical doping level for the transition is about 0.35 e/f.u., 0.25 e/f.u., and 0.12 e/f.u. for Cl, Br, and I, respectively.

Therefore, within a CNT with intrinsic charge transfer, the magnetic state of CrI_3 is nominally in the ferromagnetic state. This doping dependent switching of magnetism for CrX_3 appears in the single-chain phase, but not in its monolayer 2D phase, where the ferromagnetic ground state is not changed by doping (Supporting Figure S10). On the other hand, the magnetic energy of VX₃ chains also tends to decrease in magnitude with increased doping, but the system remains ferromagnetic for all doping ranges considered. Our calculations suggest that electrically tunable magnetism in CrX_3 single-chains can be realized by electrostatic gating of CrX_3 -filled CNTs.

Figure 4 shows the electronic structures of MX₃ single-chains encapsulated in CNTs. The Dirac point energy of CNT is pushed upward because of electron transfer from the CNT to the chains. For CrX₃, electrons transferred from the CNT populate the conduction band of the chain. Notably, with CNT encapsulation, electron doping brings the flat bands in the antiferromagnetic CrX₃ to the Fermi level, and such states are energetically well separated from the other chain-derived states.

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Those flat bands can provide an ideal system to study correlated electron physics in one dimension. For the ferromagnetic CrI₃ chain, the additional electron goes into spin-polarized conduction bands, so CrI₃ becomes a half metal. Since the isolated ferromagnetic VX₃ chains are already half-metallic, charge transfer from the CNT provides additional spin-polarized carriers to the chain.

3. CONCLUSIONS

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In conclusion, we present 1D CrX₃ and VX₃ magnetic single-chain structures via nanotube encapsulation. We demonstrate the 1D face-sharing octahedron MX₃ structure can be universally synthesized as a single-chain limit inside a nanotube. The nanotube vessel stabilizes and protects the materials, allowing access to 1D single-chain limit, specifically CrI₃, CrBr₃, CrCl₃, VI₃, VBr₃ and VCl₃. Our DFT calculations suggest that charge transfer from CNT to MX₃ single-chain plays a critical role in stabilizing the chain structures. Notably, antiferromagnetic CrX₃ chains host isolated flat bands to which electron doping can be achievable via charge transfer from the CNT. We find that magnetic states of CrX₃ chains can be switched by electron doping. These findings can pave the way for further investigations into low-dimensional magnetic systems and confinement-stabilized materials in nanotubes, which offer exciting opportunities for future research and applications across various fields.

4. Experimental Section

Materials: CNTs were purchased from Sigma-Aldrich (single-walled: 704113) and CheapTubes (90% SW-DW CNTs) and were annealed in air at 510 °C for 15 minutes prior to filling to open the end caps. The precursors utilized for filling included commercially available CrI₃ (purchased from Ossila), CrCl₃ (99.99% Sigma-Aldrich and 99.9% Alfa-Aesar), VBr₃ (99.5% Alfa-Aesar), and VCl₃ (99% Alfa-Aesar) powders, as well as synthesized CrBr₃ and VI₃ crystals. The chemical vapor transport (CVT) method was used to grow CrBr₃ and VI₃ precursors. For CrBr₃, a 1:0.8 molar ratio of Chromium (99% Alfa-Aesar) and TeBr₄ (99.9% Alfa-Aesar) was mixed with a total mass of 1g in a quartz ampule. For VI₃, a 1:3 molar ratio of Vanadium (99.7% Alfa-Aesar) and Iodine (99.99% Alfa-Aesar) was mixed with a total mass of 1g in a quartz ampule. The ampule (10 mm diameter and 15 cm long) was then sealed under high vacuum (~10⁻⁶ torr) and placed in a horizontal one-zone furnace

with the hot end at 750 °C for 5 days before being cooled to room temperature. The synthesized small crystals were extracted inside an Ar-filled glove box to minimize oxidation.

*Growing MX*₃ @ *Nanotube*: The CNTs (approximately 3 mg) were mixed with 30 mg of precursor materials and sealed in a 6 mm inner diameter and 15 cm long quartz ampule under high vacuum ($\sim 10^{-6}$ torr). The sealed ampule was then heated to 650 °C in a single-zone box furnace and kept there for 3 days before being cooled down to room temperature over 1 day. The synthesized materials (MX₃@nanotube) were dispersed in isopropanol using a bath sonicator for 15 minutes, and drop-cast onto lacey carbon TEM grids for TEM/STEM characterization.

TEM/STEM Imaging and Simulations: Initial sample screening was conducted using a JEOL 2010 microscope at 80 kV. Atomic-resolution ADF-STEM images were acquired using the double spherical (Cs) aberration-corrected JEOL ARM-200F and TEAM 0.5 at the National Center for Electron Microscopy (NCEM). The JEOL ARM-200F microscopy was set at 80 kV with a 23 mrad convergence angle and collection semiangles ranging from 40 to 160 mrad, while the TEAM 0.5 instrument was operated at 80 kV with a convergence angle of 30 mrad and collection semiangles from 37 to 187 mrad. The electron dose for atomic-resolution STEM imaging was estimated to be $\sim 1 \times 10^8 \text{ e}^-/\text{nm}^2$. The STEM images were calibrated using 3.4 Å inter-wall spacing of carbon nanotubes.

High-resolution (HR) STEM image simulations were simulated using MacTempas software based on multislice calculations. The simulation parameters were similar to the experimental parameters (e.g., a probe semiangle of 23 mrad or 30 mrad, 0.05 Å/pixel sampling, and 20 frozen phonon calculations) for each simulation. Image analysis and processing were performed using ImageJ software. Poisson noise was added for the simulated STEM images to match the experimental results.

Calculations: We performed first-principles DFT calculations as implemented in SIESTA^[20]. We used the Perdew-Burke-Ernzerhof (PBE) functional^[21], fully relativistic optimized norm-conserving pseudopotentials^[22], and a localized pseudoatomic orbital basis. Van der Waals interactions were included within the Grimme-D2 scheme^[23]. A real-space mesh cutoff of 800 Ry was used. We used a 40 Å thick cell along the transverse vacuum direction. The primitive Brillouin zone of isolated MX₃ chains was sampled by 32 k points, and the number of k points was proportionally reduced in supercell calculations. The atomic positions of MX₃ chains with and without a CNT were optimized with a force threshold of 0.01 eV/Å, while fixing the position of carbon atoms in CNT. Electron doping to the isolated chain is simulated by adjusting the total number of electrons and adding positive compensating background charges. We use the sisl package to process and plot the real-space electron density^[24]. For single-chains in CNT, The unfolded band structures are calculated in the same manner with our previous study^[10k].

Supporting Information

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

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Conflict of Interest

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The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure 1. Structure characterization of 1D CrI₃ single chain inside a nanotube. (a) Aberrationcorrected ADF-STEM image of a CrI₃ single chain encapsulated within a double-walled CNT. Scale bar: 1 nm. (b) Atomic model of face-sharing 1D MX₃ single chain within nanotube. The face-sharing MX₆ octahedra are shadowed. The transition metal atoms are displayed in blue and the halogen atoms are displayed in red. (c), (d) Experimentally observed atomic-resolution STEM images of (c) 0° and (d) 90° rotated CrI₃ single chains encapsulated inside nanotubes. Cr, I₂, and I₁ are marked by blue, yellow, and red circles, respectively. Scale bar: 0.5 nm. (e), (f) Intensity line profile along the colored line in panel (c) and (d), respectively. (g), (h) Simulated STEM images of (g) 0° and (h) 90° rotated CrI₃ single chains encapsulated inside nanotubes. Cr, I₂, and I₁ are marked by blue, yellow, and red circles, respectively. Scale bar: 0.5 nm. (e), (f) Intensity line profile along the colored line in panel (c) and (d), respectively. (g), (h) Simulated STEM images of (g) 0° and (h) 90° rotated CrI₃ single chains encapsulated inside nanotubes. Cr, I₂, and I₁ are marked by blue, yellow, and red circles, respectively. Scale bar: 0.5 nm. 12/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley com/doi/10.1002/adma.20230742 by Univ of California Lawrece Berkeley National Lab, Wiley Online Library on (27/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/adma.20230742 by Univ of California Lawrece Berkeley National Lab, Wiley Online Library on (27/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/adma.20230742 by Univ of California Lawrece Berkeley National Lab, Wiley Online Library on (27/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/adma.20230742 by Univ of California Lawrece Berkeley National Lab, Wiley Online Library on (27/10/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons



Figure 2. Universal stabilization of 1D MX₃ within a nanotube. (a-e) Experimental (left) and simulated (right) atomic-resolution STEM images of (a) CrBr₃, (b) CrCl₃, (c) VCr₃, (d) VBr₃, and (e) VCl₃, respectively. Scale bar: 0.5 nm. The positions of transition metal atoms, halogen double atoms, and halogen single atoms are marked by blue, yellow, and red circles, respectively.





Figure 3. Calculated magnetic state, charge transfer from CNT, and electron doping effects. Schematics of (a) antiferromagnetic and (b) ferromagnetic state of CrI₃ single-chains. The easy axis is along the chain direction. (c,d) Electron density transferred from the CNT to the chain. (e) Relative stability of 1D chain phase against 2D monolayer phase and (f) magnetic energy of single-chains as a function of electron doping.



Figure 4. Calculated electronic structures of single-chain MX₃ encapsulated in CNTs. (a) antiferromagnetic CrCl₃, (b) antiferromagnetic CrBr₃, (c) ferromagnetic CrI₃, and (d-f) ferromagnetic VCl₃, VBr₃ and VI₃. Supercell band structures are projected onto and unfolded with respect to the primitive Brillouin zone (PBZ) of the chain and CNT, respectively, and Z_{chain} and Z_{CNT} denote the PBZ boundaries. Black lines indicate the CNT states, and red and blue lines are majority and minority spin states of the chain, respectively.

Table1. Experimental (aexp) and calculated lattice constants (acalc) of MX₃ chains and DFT results of formation energies (E_f), easy axis, magnetic anisotropy energy (E_{MAE}) and magnetic exchange interaction parameters parallel $(J_{1,2}^{||})$ and perpendicular $(J_{1,2}^{\perp})$ to the easy axis up to the second nearest neighbors.

	aexp (Å)	a _{calc} (Å)	<i>E_f</i> (eV/atom)	Easy Axis	<i>E_{MAE}</i> (meV/f.u.)	$J_1^{ }, J_2^{ }$ (meV)	$J_1^{\perp}, J_2^{\perp} \text{ (meV)}$
CrI ₃	6.8	6.81 (FM) 6.72 (AFM)	-2.28	Z	0.41	10.8, 5.3	3.1, -1.2

CrBr ₃	6.3	6.29	-2.62	х	0.18	19.3, 4.0	9.0, -1.5
CrCl ₃	6.0	6.00	-3.01	х	0.04	25.2, 3.0	15.0, -1.2
VI ₃	6.8	6.69	-2.77	x	0.99	itinerant ferromagnetism	
VBr ₃	6.3	6.30	-3.18	z	0.20		
VCl ₃	6.0	6.04	-3.60	z	0.28		

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One-dimensional Magnetic MX₃ Single-Chains (M=Cr, V and X=Cl, Br, I)

Charge Induced Stabilization				
ndonitorior	0000000000			
Crl ₃	VI ₃			
CrBr ₃	VBr ₃			
CrCl ₃	VCl ₃			

1D magnetic van der Waals materials with composition MX₃ (M= Cr, V, and X= Cl, Br, I) confined in carbon nanotubes is investigated. Atomic-resolution scanning transmission electron microscopy (STEM) identifies unique 1D face-sharing octahedron MX₃ structure. Charge transfer from CNT to MX₃ single-chain plays a critical role in stabilizing the chain structures.