

Imprinting Ferromagnetism and Superconductivity in Single Atomic Layers of Molecular Superlattices

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Ferromagnetism and superconductivity are two antagonistic phenomena since ferromagnetic exchange fields tend to destroy singlet Cooper pairs. Reconciliation of these two competing phases has been achieved in vertically stacked heterostructures where these two orders are confined in different layers. However, controllable integration of these two phases in one atomic layer is a longstanding challenge. Here, an interlayer-space-confined chemical design (ICCD) is reported for the synthesis of dilute single-atom-doped TaS₂ molecular superlattice, whereby ferromagnetism is observed in the superconducting TaS₂ layers. The intercalation of 2H-TaS₂ crystal with bulky organic ammonium molecule expands its van der Waals gap for single-atom doping via co-intercalated cobalt ions, resulting in the formation of quasi-monolayer Co-doped TaS₂ superlattices. Isolated Co atoms are decorated in the basal plane of the TaS₂ via substituting the Ta atom or anchoring at a hollow site, wherein the orbital-selected p-d hybridization between Co and neighboring Ta and S atoms induces local magnetic moments with strong ferromagnetic coupling. This ICCD approach can be applied to various metal ions, enabling the synthesis of a series of crystal-size TaS₂ molecular superlattices.

exchange interaction tends to break the Cooper pairs in the conventional superconductors, making it intrinsically incompatible with ferromagnetism.^[8,10,11] Therefore, rational design and synthesis of novel superconducting materials integrated with ferromagnetism has been a formidable challenge. Enormous effort devoted to construct artificial systems hosting these two competing phases often involves the fabrication of vertical heterostructures with alternative stacking of 2D superconductor and ferromagnetic layers (e.g., Ni_{0.66}Al_{0.33}(OH)₂-TaS₂ and CoCp₂-SnSe₂).^[12–18] In such heterostructures, the proximity effects between superconducting and ferromagnetic layers generate many exotic properties such as magnonfluxon interaction and triplet pairing.[19-21] Alternatively, integrating these two competing phases into a single layer not only results in new exciting physics but also offers a great flexibility for the device fab-

The interplay between superconductivity and ferromagnetism creates numerous exotic physical phenomena including Majorana particles and topological superconductivity,^[1-6] which can be harnessed for next-generation superconducting spintronics and quantum computing.^[7–9] Unfortunately, the ferromagnetic rication. However, controllable synthesis of in-plane hybrid atomic layers accommodating superconductivity and ferromagnetism remains a considerable challenge. Chemical modification of 2D material surfaces has been

widely employed to tailor their electronic and magnetic

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Scheme 1. Illustration of the interlayer-space-confined chemical design (ICCD) toward the synthesis of TaS_2 inorganic/organic molecular superlattice with the superconducting regions and ferromagnetic regions in single atomic layers.

properties,^[22–25] which can be adopted to induce magnetic order in layered 2D superconductors. Conventional strategies used to modify 2D surface generally rely on post chemical treatment of exfoliated 2D nanosheets from bulk materials.^[26-29] Inevitably, these exfoliated 2D nanosheets suffer from a random distribution of various defects and layer thickness, leading to nonuniform physical characteristics. In contrast, a direct modification of layered bulk materials prior to the exfoliation via accessing its interlayer van der Waals (vdW) gap is expected to facilitate a uniform defect-free surface functionalization. In addition, as-modified bulk crystals maintain a high stability, which can be mechanically exfoliated into thin flakes with desired thickness and size for device fabrication. Therefore, developing new approach toward interlayer-space-confined modification with a rational choice of the chemical species provides possibility to integrate robust magnetic order in 2D superconductors.

To this end, we develop a new approach, namely, interlayerspace-confined chemical design (ICCD) for engineering crystalsize molecular superlattices via a simultaneous intercalation and chemical modification of bulk 2H-TaS2, whereby ferromagnetism was introduced in the TaS₂ layers with retained superconductivity (Scheme 1). The intercalation of tetrabutylammonium molecules into the interlayer space of TaS₂ expands the van der Waals (vdW) gap for a simultaneous surface modification by co-intercalated metal species, leading to the formation of TaS₂ inorganic-organic molecular superlattices with quasimonolayer characteristics and enhanced superconductivity ($T_{\rm C}$ = 3.8 K). Using cobalt as a prototype system, we demonstrate that isolated Co atoms can be co-intercalated into the vdW gap and subsequently integrated into the basal plane of TaS₂ with two adsorption configurations including replacement of Ta (Co_{Ta}) and adsorption at the hollow site (Co_{HS}). The orbital-selected

p-d hybridizations of Co atoms with neighboring Ta and S atoms induce local magnetic moments and long-range ferromagnetic coupling within the TaS₂ layer, presumably mediated through Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction. We further demonstrate that various metal ions, such as $\rm In^{3+}, Pd^{2+}$, and Fe³⁺ ions, can also be applied to produce superlattice structures with tunable interlayer modification. These crystal-size molecular superlattices exhibit high stability and retain the flexibility toward the mechanical exfoliation of microsized flakes for device fabrication.

We first grew 2H-TaS₂ single crystals as the host superconductor via chemical vapor transport (Figure S1, Supporting Information). 2H-TaS₂ single crystals were then treated in tetrabutylammonium chloride (TBAC) solution of dimethylformamide (DMF) at 110 °C to form TaS2 molecular superlattice (see the Experimental Section for details). As shown in the photograph, this treatment results in a substantial expansion of TaS₂ crystal presumably due to the intercalation of TBAC molecules (Figure S2a,b, Supporting Information). X-ray diffraction (XRD) analysis (Figure 1a) reveals that pristine 2H-TaS₂ crystal with a P63/mmc symmetry displays a set of (00l) diffraction peaks along the *c*-axis (yellow line), corresponding to interlayer distance of ≈6.05 Å. In contrast, TBAC-treated TaS₂ crystal (TBAC-1) does not show any diffraction peak, presumably due to the disruption of the coherent layer stacking arising from the dramatic expansion of bulk crystal.

ICCD method developed here involves a controlled TBAC intercalation with interlayer-space-confined chemical modification of TaS_2 via co-intercalated metal ions. To demonstrate this concept, we first dissolved $CoCl_2$ salt into the TBAC-DMF to form a mixed Co-TBAC-DMF solution (see the Experimental Section for details). Unexpectedly, well-ordered TaS_2

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Figure 1. Structural characterizations of TaS_2 molecular superlattice. a) XRD patterns of TaS_2 crystals intercalated with tetrabutylammonium molecules mixed with different concentrations of Co^{2+} ion. The yellow line refers to the pristine 2H-TaS₂ crystal; the purple line (TBAC-1) refers to the intercalated TaS_2 crystal using the TBAC-DMF solution without Co^{2+} ion; the blue (Co-TBAC-1) and green (Co-TBAC-2) lines refer to the intercalated TaS_2 crystal using the TBAC-DMF solution with a Co^{2+} ion concentration of 0.005 and 0.03 M, respectively. b–f) Typical TEM (b), high-resolution TEM (c), selected-area electron diffraction (d), cross-sectional TEM (e), and AFM (f) images of exfoliated TaS_2 superlattice nanosheets. h) Low-magnification HAADF-STEM image and elemental mapping of S-K, Ta-M, and Co-K edges of a single TaS₂ superlattice nanosheet. i) Schematic diagram of the TaS₂ molecular superlattice modified by Co, In, Pd, and Fe.

molecular superlattice can be formed by optimizing the concentration of Co^{2+} ions. At a low Co^{2+} concentration of 0.005 M, as-treated TaS₂ crystal (Co-TBAC-1) shows a pronounced expansion (Figure S2c,d, Supporting Information) without XRD diffraction peak. When Co^{2+} ion increases to 0.03 M, Co-TBAC-treated TaS₂ crystal does not exhibit significant expansion but possesses a new set of (001) diffraction peaks located at lower angles due to a well-ordered intercalation of TaS₂ crystal with interlayer spacing of 9.9 Å (Figures S2e,f and S3, Supporting Information). Raman measurements reveal that the TaS₂ molecular superlattice maintains 2H phase (Figure S4, Supporting Information).

TaS₂ molecular superlattices can be readily exfoliated into ultrathin flakes under ultrasonication and dispersed in the solvent (Figure S5, Supporting Information). Figure 1b depicts a typical transmission electron microscopy (TEM) image of as-exfoliated TaS₂ superlattice nanosheets with a lateral size of several micrometers. High-resolution TEM (HRTEM) image of this flake shows a perfect 2D lattice fringes with interplanar spacing of \approx 2.87 Å (Figure 1c), corresponding to (100) plane of 2H-TaS₂. The electron diffraction (Figure 1d) reveals a series of sharp spots with well-defined hexagonal symmetry attributed to a high crystallinity of the TaS₂ layers. Cross-section TEM image of \approx 9.9 Å (Figure 1e)





and Figure S6, Supporting Information), consistent with the XRD results. This suggests the formation of inorganic–organic hybrid TaS_2 superlattice with alternative stacking of TaS_2 and TBAC molecule layers. It is noted that the TaS_2 molecular superlattice can also be mechanically exfoliated to microsized atomic layers with variable thickness (Figure 1f and Figure S7, Supporting Information), crucial for device fabrication with high-quality flakes.

To gain insights into the interlayer-space-confined modification of such a molecular superlattice, we performed energy dispersive spectroscopy (EDS) to probe its chemical composition. Apart from the dominant Ta and S signal, EDS also reveals the presence of Co species in the superlattice nanosheets. This is evidenced by two discernible peaks located at ~0.8 and 6.9 keV, which can be assigned to Co L-edge and Co K-edge (Figure 1g). The molar ratio (W_M) between Co and Ta is determined to be ~3.4% using inductively coupled plasma optical emission spectrometry (Table 1 in the Supporting Information). Furthermore, the EDS mapping shows that all the elements (S, Ta, and Co) are distributed across the whole nanosheet evenly, suggesting a uniform Co decoration of the basal plane of TaS₂ in the superlattice (Figure 1h). Interestingly, we also found that this ICCD can be expanded to different metal ions including InCl₃, PdCl₂, and FeCl₃ toward the fabrication of a wide range of metal-modified superlattices. All these superlattices can be exfoliated into ultrathin nanosheets, which exhibit similar interlayer spacing of \approx 9.8 Å as revealed by TEM image and cross-sectional HRTEM (Figure S8, Supporting Information). The elemental analysis reveals the presence of In, Pd, and Fe elements in the corresponding superlattice nanosheets, suggesting a successful interlayer-space modification with these metal ions (Figure 1i).

To probe magnetic property of Co-decorated TaS_2 , we performed magnetization measurements using a commercial superconducting quantum interference device. As shown in **Figure 2**a, the temperature dependence of magnetic



Figure 2. Superconductivity and ferromagnetism in the Co–TaS₂ molecular superlattice. a) Temperature dependence of the magnetization (M–T curve) of the Co–TaS₂ superlattice under magnetic field of 10 Oe for ZFC and FC processes. b,c) Isothermal magnetization curves (M–H curves) at 5 and 2 K. d) AFM topographic image of a single exfoliated Co–TaS₂ superlattice nanoflake on SiO₂/Si substrate. e,f) MFM phase and amplitude images of the Co–TaS₂ nanoflake acquired at the lift height of 20 nm. g) AFM image of the four-probe device. h) Resistance of the TaS₂ superlattice as a function of temperature under perpendicular magnetic fields from 0 to 0.7 T. i) Field dependence of resistance at a fixed temperature of 1.5 K.

susceptibility (*M*–*T* curve) was measured from 300 to 2 K under both zero-field-cooling (ZFC) and field-cooling (FC) processes. Both ZFC and FC curves capture a steep decrease of susceptibility below the critical temperature (T_c) of \approx 3.8 K, attributed to the diamagnetism arising from the Meissner effect. In contrast to the quench of superconductivity observed in iron-doped NbSe₂ crystals, our observations suggest that Co–TaS₂ superlattices remain superconducting below T_c , presumably due to a strong spin–orbital scattering.^[30,31]

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It is worth noting that T_c of 2H-TaS₂ increases as the thickness decreases, in stark contrast to other 2D superconductors.^[32,33] T_c of as-prepared TaS₂ superlattice is determined to be 3.8 K, reaching the highest T_c of monolayer TaS₂ reported. This indicates that molecular intercalation of TaS₂ leads to electronic decoupling between adjacent TaS₂ layers and thus creates quasi-monolayer characteristics in the bulk superlattice.^[34] To the best of our knowledge, the T_c of bulk superlattice (3.8 K) is even higher than that of mechanically and liquid-exfoliated TaS₂ monolayers in the previous reports. This may be attributed to a higher environmental stability of TaS₂ superlattice than monolayer TaS₂ samples exfoliated by other approaches. Therefore, as-synthesized TaS₂ molecular superlattice not only shows the quasi-monolayer behaviors with highest T_c but also possesses high stability, appealing for device fabrication and practical applications.

To further study the magnetism of Co-TaS₂ molecular superlattice, we carried out the temperature-dependent isothermal magnetization. The observation of ferromagnetism in the same TaS₂ samples was demonstrated based on the fielddependent magnetization curves (M-H) collected at 5 and 2 K. The M-H curve acquired at 5 K (Figure 2b) shows an "S" shape with an obvious hysteresis loop, suggesting a ferromagnetic state in the Co-TaS₂ superlattice. Furthermore, M-H curve at 2 K (Figure 2c) reveals the ferromagnetic state in the superconducting Co-TaS₂ superlattices. In the low field regime, the system exhibits a superconducting diamagnetism with a butterfly loop. In the high field regime, ferromagnetic behavior gradually emerges. Such a superconductivity accompanying with ferromagnetic state was not observed in iron-doped TaS₂ crystal, presumably due to a low Fe content.^[30] The saturation magnetization (M_s) at 2 K is about 0.083 emu g⁻¹. The magnetic moment of individual Co atoms in TaS2 is determined to be 0.11 $\mu_{\rm B}$ derived from the following equation

$$M(\text{Co}) = \frac{M_{\text{s}}M}{\mu_{\text{B}}N_{\text{A}}} / W_{\text{M}}$$
(1)

where M_s is the saturation magnetization, M is the molar mass, μ_B is the Bohr magneton (9.274 × 10⁻²¹ erg G⁻¹), N_A is the Avogadro constant (6.02 × 10²³), and W_M is the molar ratio of Co and Ta in the superlattice. Besides, the hysteresis loop retains even at room temperature (Figure S9, Supporting Information), demonstrating a robust ferromagnetism in Co-modified TaS₂ superlattice.

Furthermore, we also used magnetic force microscopy (MFM) to characterize the magnetic response of individual exfoliated Co–TaS₂ superlattice nanoflake. Figure 2d–f and Figure S10 in the Supporting Information show the atomic force microscopy (AFM) topographic image, MFM phase, and

amplitude images of the Co-TaS₂ nanoflake on a SiO₂/Si substrate acquired at the lift height of 20 nm. In contrast to the SiO₂ substrate, we observed a noticeable negative phase shift of -160 milli-degree (m^o) and a positive amplitude shift of 349 μ V for the Co–TaS₂ nanoflake (refer to the line profile in Figure S10, Supporting Information), suggesting the ferromagnetic property of Co-TaS2 nanoflake.^[35] In addition, MFM measurements reveal a decrease of negative phase shift with an increase of lift height, which further proves the presence of the ferromagnetism of Co-TaS₂ nanoflake (Figure S11, Supporting Information).^[35,36] Notably, the MFM phase and amplitude images show a uniform magnetic signal in the whole nanoflake, suggesting the presence of ferromagnetism in the superconducting TaS₂ layers. Similar results were observed for Co-TaS2 nanoflakes with different thickness (Figure S12, Supporting Information). Therefore, our MFM measurements confirm a relatively uniform distribution of ferromagnetic phase in the whole Co-TaS₂ nanoflake with different thicknesses.

In addition, we also performed low-temperature transport measurement of mechanically exfoliated TaS₂ superlattice nanoflakes to further probe its superconducting behavior. Asexfoliated flake with thickness of ≈21 nm was patterned into a four-probe device with Cr/Au electrodes using e-beam lithography (Figure 2g and Figure S13, Supporting Information). The temperature dependence of resistance under perpendicular magnetic fields was displayed in Figure 2h. At zero magnetic field, the resistance shows a sharp superconducting transition at 3.8 K, consistent with the magnetic measurements. An increase of magnetic field not only shifts T_c toward lower temperature but also broadens the superconducting transition. The superconductivity is completely suppressed under magnetic field of ≈ 0.7 T. This superconducting character is further verified by monitoring the resistance versus magnetic field at 1.5 K. As depicted in Figure 2i, zero-resistance persists up to 660 Oe, above which the resistance increases monotonously and saturates around 0.7 T.

We then probed the atomic structure of Co-TaS₂ molecular superlattices using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The Z contrast of HAADF-STEM image of Ta, Co, and S follows this trend Ta > Co > S, which allows us to identify their atomic positions in the thin flakes.^[37] Figure 3a shows a typical widefield view of HAADF-STEM image of the Co-TaS₂ monolayer with 1H trigonal symmetry. The brightest spots correspond to Ta atoms while the S atoms are barely resolved in the HAADF image. Apart from these features, we also observed some less bright spots marked by white circles, corresponding to the isolated Co atoms within the TaS₂ layer. A close-up HAADF-STEM image reveals two different Co sites including substitution of Ta by Co atom (marked by green circle, Co_{Ta}) and adsorption of Co at the hollow site (marked by blue circle, Co_{HS}) of TaS₂ basal plane (Figure 3b). Additional HAADF-STEM images acquired from different monolayer Co-TaS2 samples are presented in Figure S14 in the Supporting Information. Moreover, the simulated HAADF-STEM images of these two density functional theory (DFT)-optimized Co configurations (Figure 3d,g) show good agreement with the experimental data in Figure 3c,f. In both cases, Co dopant can maintain the trigonal prism symmetry (Figure 3e,h), which may favor the spin ordering within







Figure 3. Probe atomic structures of the Co dopants in the Co–TaS₂ monolayer. a) HAADF-STEM image of the basal plane of Co–TaS₂ monolayer. b) Magnified HAADF-STEM image of the basal plane of Co–TaS₂ monolayer. c) HAADF-STEM image for the substitution site of the Co atom (Co_{Ta}). d) HAADF image simulation for the Co_{Ta} site. e) DFT-optimized atomic model of substituted Co site in the TaS₂ lattice. f) HAADF-STEM image for the hollow site of Co atom (Co_{HS}). g) HAADF-STEM image simulation for Co_{HS} site. h) DFT-optimized atomic model of hollow Co site.

TaS₂ basal plane, as will be discussed later. In addition, X-ray absorption fine structure measurements further confirm the absence of aggregated Co clusters in our samples (Figure S15, Supporting Information).

To explore the origin of the ferromagnetism in the Co–TaS₂ superlattice, we first calculated the spin-polarized electronic structures of individual Co dopants for these two configurations: Co_{Ta} and Co_{HS} in monolayer TaS₂ (see details in the Experimental Section). In contrast to the nonmagnetic nature of pristine 2H-TaS₂ (Figure S16, Supporting Information), Co-doped TaS₂ shows the spin-polarization density of states (DOS). As shown in Figure S17 in the Supporting Information, Co_{Ta} -TaS₂ clearly shows an asymmetric distribution of spin-up and spin-down DOS near the Fermi level. The projected density of states (PDOS) reveals spin-polarized states mainly arises from the 3d states of Co atom, 3p states of six nearest-neighboring Ta atoms in

TaS₂ lattice. The spin density of Co shows the opposite orientation compared to that of nearest-neighboring S and Ta atoms (**Figure 4a**). The magnetic moment of Co, six nearest S, and Ta atoms is determined to be -1.3, 0.7, and 0.08 $\mu_{\rm B}$, respectively, which gives rise to a net spin of $\approx 0.52 \,\mu_{\rm B}$ for each Co_{Ta} site. The crystal field of Co and Ta atoms in monolayer TaS₂ (Figure 4c) splits the d states of Co and Ta atoms into three groups, namely, a single $a_1 (d_{z}^2)$ orbital and two doubly degenerate $e_1 (d_{xy/x}^2 - \gamma^2)$ and $e_2 (d_{xz/yz})$ orbitals.^[38] The orbital resolved PDOS (Figure 4d) shows that the spin density is mainly attributed to the $d_{xy/x}^2 - \gamma^2$ and $d_{xz/yz}$ orbitals of Co, p_z orbital of S, and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms in the energy range of -1.5 to -0.7 eV and 0.2 to 0.6 eV. This indicates that the induced magnetic moments on the nearby S and Ta atoms is due to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xz/yz}$ orbitals of Ta atoms is further the groups of the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xz/yz}$ orbitals of Ta atoms is for substituted Co with p_z orbital of S and $d_{xy/x}^2 - \gamma^2$ and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms is further to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xz/yz}$ orbitals of Ta atoms is due to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms is further to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms is due to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms is due to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms is due to the hybridization of $d_{xy/x}^2 - \gamma^2$ and $d_{xy/x}^2 - \gamma^2$ orbitals of Ta atoms (Figure 4e).

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Figure 4. The origin of the ferromagnetism in the $Co-TaS_2$ layers. a) Spin density of TaS_2 monolayer with the Co dopant-substituted Ta site and b) anchored at the hollow site. c) Schematic illustration of 1H lattice symmetry of a monolayer TaS_2 . d) Total DOS of a substituted Co and neighboring six S and Ta atoms in TaS_2 monolayer, and the corresponding orbital-resolved PDOS. e) Schematic images of the d orbitals of Ta and Co and p_z orbital of S. f,g) Spin density plot of TaS_2 monolayer with two substituted Co atoms and two Co atom over hollow sites.

In contrast to Co_{Ta} case, the spin density of Co_{HS} -TaS₂ (Figure S18, Supporting Information) is primarily contributed by the 3d states of Co atom and 5d states of three nearest-neighboring and three second-neighboring Ta atoms in TaS₂ layer. Spin density over these atoms show the same orientation (Figure 4b). The orbital-resolved PDOS (Figure S19, Supporting Information) reveals that the hybridization between d_z^2 orbitals of Co_{HS} and these six neighboring Ta atoms induces the spin density over Ta sites. The magnetic moment of Co_{HS}, three nearest-neighboring, and second-neighboring Ta atoms

are predicted to be 1.9 $\mu_B,$ 0.3 μ_B and 0.1 $\mu_B,$ respectively, giving rise to a large net spin of 2.3 $\mu_B.$

The magnetic coupling of the localized magnetic moments is characterized by their spin exchange interactions. To investigate the possible magnetic coupling between adjacent dopant sites, we then calculated a supercell containing two Co atomic sites including three configurations: SS (two nearby Co_{Ta} sites), HH (two nearby Co_{HS} sites), and SH (one Co_{Ta} site and one Co_{HS} site). The Co–Co distance in this model is about 10, 8.8, and 5.8 Å for SS, HH, and SH configurations,





respectively, close to the minimal spacing between two Co sites captured by STEM. DFT calculations predict that the FM coupling between two Co sites is more energetically favorable compared to AFM coupling, lower in energy by 200, 50, and 2 meV for SS, HH, and SH configurations, respectively. The spin density plot shows that the majority of spin still localizes around the Co atoms and neighboring Ta and S atoms (Figure 4f,g and Figure S20, Supporting Information) with negligible spin density distribution between these two Co sites. This indicates that a direct exchange coupling between two induced magnetic moments is not likely to occur here. Instead, ferromagnetic coupling between Co-induced magnetic moments in TaS₂ layer may arise from an indirect spin exchange interaction, namely, the RKKY interaction.[39-41] The RKKY interaction is mediated through the polarization of conduction electrons surrounding the local magnetic moment. In this scenario, adjacent magnetic moments are coupled through the itinerant electrons, leading to a longrange spin exchange interaction. A high carrier density in the metallic 2H-TaS₂ host also favors the spin exchange interactions between two isolated Co atoms through the RKKY mechanism.

The observation of ferromagnetism in the same Co-TaS₂ samples with retained superconductivity can be explained by these possible physical pictures including i) the presence of the electronic phase-separated domains in the same TaS₂ layer or ii) the survival of superconductivity in the region close to the ferromagnetically coupled Co dopants. Due to a diluted dopant concentration, it is very likely that the presence of inplane phase-separated domains leads to the observation of two competing phases in the same TaS₂ atomic layers. At the microscopic scale, ferromagnetic states reside in the regions near Co atoms and superconductivity stems from the regions away from the ferromagnetic Co centers (Scheme 1). A relatively uniform distribution of Co dopants results in uniform magnetic signal observed over the whole flakes at the macroscopic scale. A detailed future study is required to probe whether the novel superconducting states such as the Yu-Shiba-Rusinov state or nonzero total momentum pairs exist in the regions near the Co center.^[8,42]

In summary, we have developed a new chemical functionalization strategy, namely, ICCD of bulk crystals toward the fabrication of single-atom-doped TaS₂ molecular superlattice with the introduction of ferromagnetism in superconducting TaS₂ single layers. The intercalation of 2H-TaS2 crystal with bulky organic ammonium molecule opens up its vdW gap for singleatom doping of TaS2 via co-intercalated cobalt ions, resulting in the formation of monolayer Co-decorated TaS₂ molecular superlattice. Atomically dispersed Co atoms integrated to the basal plane of TaS2 induce the spin polarization due to the orbital-specific p-d hybridization with neighboring Ta and S atoms, whereby ferromagnetic coupling between adjacent sites is presumably due to the indirect RKKY spin exchange interactions. Furthermore, this ICCD approach can be applied to various metal ions, producing a series of molecular superlattices with tailored properties. Our findings provide a new chemical route to engineer artificial molecular superlattice of layered materials with exotic and antagonistic properties for desired functionalities.

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.

Keywords

2D superconductivity, ferromagnetism, inorganic-organic superlattices, interlayer modification, single atoms

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