Tip-induced excitonic luminescence nanoscopy of an atomically resolved van der Waals heterostructure

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The electronic and optical properties of van der Waals heterostructures are strongly influenced by the structuration and homogeneity of their nano- and atomic-scale environments. Unravelling this intimate structure–property relationship is a key challenge that requires methods capable of addressing the light–matter interactions in van der Waals materials with ultimate spatial resolution. Here we use a low-temperature scanning tunnelling microscope to probe—with atomic-scale resolution—the excitonic luminescence of a van der Waals heterostructure, made of a transition metal dichalcogenide monolayer stacked onto a few-layer graphene flake supported by a Au(111) substrate. Sharp emission lines arising from neutral, charged and localized excitons are reported. Their intensities and emission energies vary as a function of the nanoscale topography of the van der Waals heterostructure, explaining the variability of the emission properties observed with diffraction-limited approaches. Our work paves the way towards understanding and controlling optoelectronic phenomena in moiré superlattices with atomic-scale resolution.

Van der Waals (vdW) heterostructures made from stacks of two-dimensional (2D) materials, particularly semiconducting transition metal dichalcogenides (TMDs), are ideal systems for studying fundamental phenomena related to tightly bound electron-hole pairs (excitons) and their exploitation in atomically thin optoelectronic devices. The rich physics of excitons, trions (that is, charged excitons), and more complex many-body states has been addressed in TMDs and related vdW heterostructures through optical spectroscopy, particularly by recording their micro-photoluminescence (μPL) characteristics, with a diffraction-limited spatial resolution of typically ≤1 μm. These far-field optical studies have highlighted substantial spatial variations in the optical response of a given sample, due to inhomogeneities of the nanoscale environment, including strain gradients, dielectric disorder, localized defects and dopants. Taking advantage of these subtle structure–property relationships, periodic nanoscale moiré super-potentials resulting from the controlled rotational mismatch between stacked 2D layers have recently been used to tailor exciton physics, with potential outcomes for quantum simulation and quantum technologies. Understanding of such emergent phenomena requires addressing excitons and their local environment with a spatial resolution below the moiré wavelength (≤10 nm) and the exciton Bohr radius (~1 nm) (ref. 9), that is, two to three orders of magnitude below the optical diffraction limit.

Recently, attempts have been made to address excitons in TMDs with nanoscale resolution. In particular, tip-enhanced photoluminescence (PL) microscopy has been used to image strain gradients with a resolution of ~15 nm. In parallel, atomically resolved luminescence has been reported on single molecules using scanning-tunnelling-microscopy-induced luminescence (STML). The STML measurement consists of recording—in the far field—the light emitted at the scanning tunnelling microscope (STM) tip–sample junction under the application of a constant tunnelling current. This
method was recently applied to investigate excitonic emission from TMDs in ambient air\cite{21,22}. Under these conditions, atomic-scale resolution could not be attained, probably because of contamination and lack of mechanical and thermal stability. Attempts to address the excitonic properties of TMDs with STM in an ultrahigh vacuum at cryogenic temperatures have been reported\cite{21,22}, but the radiative recombination of excitons and trions was probably quenched by the strong interaction with the supporting metallic substrate\cite{23}.

In this Article, we demonstrate excitonic luminescence from a 2D semiconductor with nanoscale resolution provided by low-temperature STML. We show that a vdW heterostructure based on a TMD monolayer, decoupled from an Au(111) crystal by a few-layer graphene flake (FLG), allows for the preservation of its luminescence and ensures optimal STM imaging of surface atoms and moiré superlattices. Our results provide insights into the mechanisms leading to STM-induced luminescence in vdW heterostructures and further establish STM-based methods as a unique tool to correlate the optical response of low-dimensional systems to their nano- and atomic-scale environments.

**Sample design and μPL mapping**

Our measurements were performed on a vdW heterostructure made of a molybdenum diselenide (MoSe$_2$) monolayer stacked on top of a few layers (ranging from three to five) of FLG deposited onto a Au(111) substrate\cite{24} (Methods and Supplementary Section 1). Figure 1a–c shows a schematic of the STML experiment, an optical image of the MoSe$_2$/FLG/Au(111) heterostructure and an atomically resolved constant-current STM image, respectively. Here, akin to hexagonal boron nitride\cite{25}, the FLG provides a smooth substrate for the TMD and ensures electrical conduction. This configuration also uses the plasmonic properties of the Ag tip–Au substrate junction (Fig. 1a), which enhances radiative recombination in STML experiments\cite{26}.

We first report on the low-temperature μPL measurements recorded ex situ using a laser beam of ~1 μm diameter at various close-lying spots on the sample (Fig. 1b). The strikingly different μPL spectra (Fig. 1d) suggest sizeable inhomogeneities at the sub-micrometre scale. These inhomogeneities probably stem from thermal annealing performed before introducing the sample into the STM chamber (Methods).

Four main types of low-temperature μPL spectrum are identified on the MoSe$_2$/FLG/Au region (Fig. 1b and Supplementary Section 2). First, we observe the spectra dominated by a high-energy emission line near 1.65 eV, followed by a lower-intensity feature, about 30 meV below the main line (Fig. 1d, triangle). The main and lower-energy lines are assigned to the bright neutral exciton (X$^0$) and negative trion (X$^-$), respectively\cite{27}. The negatively charged nature of the trion will be discussed below. Next, we also observe spectra that only display emission from the X$^0$ line (Fig. 1d, square), as well as more complex spectra, showing several sharper, spatially dependent and spectrally diffusing features assigned to localized excitons\cite{28}, with possible contributions from (X$^0$, X) pairs stemming from the nanoscale regions subject to distinct local strain fields (Fig. 1d, circle). Finally, redshifted X$^0$ lines below 1.60 eV are also observed (Fig. 1d, star). These behaviours are directly related to the quality of MoSe$_2$/FLG and FLG/Au interfaces. When MoSe$_2$ and FLG are tightly coupled, we expect an efficient filtering effect to take place\cite{29,30}, which yields single-line spectra akin to the trace marked with square (Fig. 1d). Hence, the observation of X$^0$ and X emission (Fig. 1d, triangle) suggests partial decoupling between the top MoSe$_2$ layer and the FLG/Au underneath. Dominant emission from localized states (Fig. 1d, circle) may stem from the local conformation of MoSe$_2$ to the underlying substrate made rougher by thermal annealing, as also observed in μPL measurements on MoSe$_2$ monolayers deposited onto a polycrystalline Au film\cite{31}. Finally, the large excitonic redshifts (Fig. 1d, star) are assigned to tensile strain due to the coupling between MoSe$_2$, FLG and the underlying Au substrate (Supplementary Section 2).

**STM-induced excitonic luminescence**

In such an heterogeneous landscape, STM allows probing the topography and luminescence from a localized area with a resolution down to the atomic scale. A typical STML spectrum recorded with the STM tip positioned on top of the atomically resolved region of the

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**Image Descriptions**

Fig. 1 | STM-induced luminescence of MoSe$_2$/FLG/Au(111) heterostructure.

- **a.** Sketch of the STML experiment. Tunnelling electrons (black discs) may generate an exciton (bound electron-hole pair, sketched with red and blue discs), which may recombine by emitting a photon (wavy red arrow). The red halo corresponds to the plasmonic enhancement at the tip–sample junction.

- **b.** Optical microscopy image of the sample. The monolayer of MoSe$_2$ is highlighted in red and the FLG in black, whereas the underlying Au(111) covers the rest of the image. A. Atomically resolved constant-current STM image (V = −1.3 V and I = 10 pA) of the heterostructure surface. D. Normalized μPL spectra acquired on the different points of the heterostructure shown in b. E. STM spectrum recorded on MoSe$_2$/FLG/Au(111) in the cross-marked area in c, with V = −2.8 V and I = 90 pA. The labels X$^0$, X$^-$ and X$^{-}$ in d and e denote the neutral, negatively charged and localized excitons, respectively. The FWHM of the X$^0$ line is denoted as $\gamma$.

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**Supplementary Information**

- Methods
- Supplementary Section 1

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**Author Contributions**

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**Additional Information**

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MoSe₂/FLG/Au heterostructure (Fig. 1c) is shown on Fig. 1e. This spectrum is characterized by a prominent emission line at 1.659 ± 0.001 eV with a lower-intensity feature at 1.630 ± 0.001 eV. These two lines have a full-width at half-maximum (FWHM) of 11 and 14 meV, respectively. A comparison with the μPL spectra discussed above allows assigning the high- and low-energy emission lines to X₀ and X⁻, respectively. This spectrum, along with the data discussed in Figs. 2–4, provide the sharpest emission lines achieved in STML measurements on TMDs and the first example where excitonic luminescence is obtained with the stability and cleanness required for atomically resolved imaging of the TMD atomic registry. We also note that the FLG interlayer preserves the low-temperature luminescence yield of MoSe₂, that would otherwise be massively reduced by non-radiative decay channels to the underlying Au substrate²⁹,³²,³³.

The X₀ FWHM fit from our STML spectra reaches values as low as 2.9 meV (Fig. 2e), translating into an exciton homogeneous lifetime of ~230 fs. The typical radiative lifetimes are 2 ps in hexagonal-boron-nitride-capped monolayer MoSe₂, deposited onto a transparent substrate²⁹. Thus, the STML linewidth may be understood as a reduced X₀ lifetime due to electronic coupling between MoSe₂ and FLG/Au, with additional contributions from Purcell enhancement, due to the plasmonic STM tip–sample junction²⁶.

We estimate a quantum yield of ~10⁻⁷ photon/electron (assuming a detection efficiency of ~10%)—a value that is orders of magnitude lower than for STML experiments on single molecules³⁴. This low-emission yield suggests an efficient non-radiative exciton decay, possibly due to the quenching of hot excitons by graphene, before their relaxation down to the light cone³⁵–³⁷. Alternatively, it may reflect an intrinsically weak exciton formation probability.

### Probing an inhomogeneous nanoscale environment

STML can be used to identify inhomogeneities occurring at the scale of atoms up to a few hundreds of nanometres, and determine how they affect radiative recombination. To this end, we first recorded an STM image (Fig. 2a) on a typical area of the heterostructure that approximately corresponds to the area covered by a diffraction-limited laser spot. This image displays flat areas separated by ripples, folds and protrusions (Fig. 2a, arrows) that stem from the conformation of the heterostructure to the substrate. These so-called nano-bubbles, typically 1 nm high and 10 nm wide³⁸, correspond to areas where the TMD and FLG are slightly decoupled, most probably because of the remaining organic adsorbates at the interfaces among MoSe₂, FLG and Au. A pseudo-three-dimensional image of a typical protrusion located next to a flat area is provided in Fig. 2b.

The STML spectrum acquired on the flat area (Fig. 2c, orange) is characterized by an X₀ line at 1.590 ± 0.001 eV and by the absence of trion emission. The X₀ energy Eₓ₀ is lower than the STML spectrum (Fig. 1e), suggesting a sizeable tensile strain (Fig. 1d, star). Approximately 5 nm away, on top of the nano-bubble, the X₀ emission (in blue) is almost six times brighter, indicating reduced quenching by the underlying FLG. This spectrum displays an additional peak below the X₀ line, whose redshift (40 meV) is appreciably larger than the X⁻ binding energy (~30 meV; Fig. 1e). Since our sample is only weakly doped (Fig. 4a), this peak cannot be assigned to a charged exciton involving charge carriers at ~10 meV above the conduction band edge. It is, therefore, tentatively assigned to excitons localized near defects (X₁) (ref. ²⁸). Similarly, the STML spectra are strongly altered near larger heterogeneities such as ruptures and folds. An example is provided in Fig. 2d, where one observes a rupture in the heterostructure (blue cross) next to a flat area (orange cross). In the flat region, the STML spectrum is again characterized by a single, narrow emission line (2.9 meV FWHM; Fig. 2e) assigned to X₀. In contrast, the rupture region displays a complex spectrum, where several narrow (~700 μeV) resonances below the X₀ emission appear, probably arising from localized excitons²⁸. Similar lines have been attributed to optically active quantum dots that behave as single-photon sources³⁹–⁴¹. Overall, the data shown in Fig. 2 indicate that the μPL spectra spatially average the emission features from the nanoscale regions having distinct spectral responses and emission yields, a complexity that we are able to address owing to the nanometre resolution of STML.

### STML on atomically resolved areas

Next, we evaluate how the atomic-scale landscape affects excitonic emission from the MoSe₂ monolayer. In Fig. 3a–c, we show atomically
resolved STM images of three flat regions of the heterostructure, separated by several nanometres from one another. The STM spectra (Fig. 3d) have been acquired in each region for the tip positions indicated in Fig. 3a–c. In Fig. 3a, the STM image reveals the atomic structure of the TMD as well as bright and dark regions indicating smooth height modulation over several nanometres. Here the STML spectra are not appreciably affected by these modulations, and are characterized by typical X₀ and X⁻ emission lines. In Fig. 3b,c, we distinguish a moiré pattern, suggesting a better quality of the MoSe₂/FLG interface than in Fig. 3a, consistent with the reduction in excitonic linewidth from 11 meV (Fig. 3a) to 9 meV (Fig. 3b) and 4 meV (Fig. 3c). The moiré period of 0.95 ± 0.02 nm (Fig. 3c) corresponds to a twist angle of 3.1° ± 0.3° between the MoSe₂ and FLG layers (Supplementary Section 3).

A smoother interface may also favour charge redistribution from the TMD to FLG flake, explaining the absence of X⁻ emission in Fig. 3b. Noteworthy, within a given nanoscale area, the STML spectra do not depend on the position of the tip with respect to the moiré pattern (Fig. 3c). Since the moiré period is slightly smaller than the typical exciton Bohr radius in TMDs (aₓ ≳ 1 nm)³⁸, possible moiré-induced spatial modulations of Eₓ₀ average out.

Two emission lines, separated by only 20 meV, are observed in the area imaged in Fig. 3c (Fig. 3d, dark yellow symbols). The X₀ line is strongly redshifted by 70 meV with respect to the data in Fig. 3a. Here an interpretation in terms of defect-induced emission can be ruled out as no atomic defects are imaged in Fig. 3c. We tentatively attribute this redshift to a combination of dielectric screening and tensile strain. Indeed, dielectric screening may redshift the excitons by several tens of millielectronvolts, as documented in TMD/graphene heterostructures. In addition, sample annealing may lead to microscopic protrusions in the Au substrate where tensile strain develops, as well as preserving excellent interfacial coupling, as testified by the observed moiré superlattice. This tightly coupled MoSe₂/FLG/Au stack may favour charge transfer from the TMD to FLG and Au substrate, a situation that prevents substrate-mediated charge transfer from MoSe₂ and trion formation. The data in Fig. 3 hint towards a key role of the MoSe₂/FLG and FLG/Au interfaces.

**STML mechanism**

Finally, we jointly address the dependence of tunnelling current and STML spectra on the tip–sample bias V at the same sample spot. The exciton binding energy Eₓ₀ can, in principle, be estimated from the difference between the local electronic gap inferred from scanning tunnelling spectroscopy (STS) measurements and the optical gap determined by Eₓ₀. Figure 4a,b displays a differential conductance (dI/dV) spectrum and STML spectra recorded with increasing bias voltage, respectively. An electronic gap of 2.17 ± 0.04 eV is deduced from the STML spectrum (Supplementary Section 4), with onsets of the valence and conductance bands at −1.68 ± 0.03 and 0.49 ± 0.01 V, respectively, indicating weak n doping. This doping allows us to identify the trion introduced in Figs. 1–3 as negatively charged. As shown...
by the STML spectra in Fig. 4b, $E_{X0} = 1.637$ eV, leading to an energy difference of $533 \pm 40$ meV that is close to the value estimated on a similar system using a combination of STS and μPL. This value is, however, much larger than the state-of-the-art optical measurements of the excitonic binding energy ($E_b$) that converge towards 220 meV in hexagonal boron nitride-capped monolayer MoSe$_2$ (ref. 15) and $-150$ meV in hexagonal boron nitride-capped MoSe$_2$/1LG (ref. 29), respectively. Our data demonstrate that the inconsistency between the determinations of $E_b$ based on the difference between the STS gap and $E_{X0}$ versus all-optical measurements$^{37}$ does not stem from spatial inhomogeneities, as both STS and optical measurements are local in our approach. We believe that the overestimation of $E_b$ originates from the fact that higher-energy electronic states near the centre of the Brillouin zone of MoSe$_2$ (I) contribute more to the STS spectrum than the large in-plane momentum states at its edges (K and K$'$), which define the direct electronic gap in TMD monolayers$^{41}$.

A combined analysis of the STS and STML spectra provides key insights into the STML mechanism. First, no STML could be observed under positive $V$. Second, from Fig. 4b, one can deduce an $X_0$ emission onset at $V_0 \approx -1.7$ V. Comparing the integrated intensity of the $X_0$ line as a function of $V$ with the $dI/dV$ spectrum (Fig. 4a, dots) reveals that the STML onset matches well with the onset of the positively charged (hole) resonance of the TMD (HR), suggesting that hole injection from the tip is a preliminary step towards excitonic luminescence. In Fig. 4c, we propose a simple mechanism inspired by a many-body approach developed to interpret the STML data of molecules$^{42}$. Originally in its ground state (GS) (used as the origin of the energy scale), the system is approximated as a two-level system, where the low-energy level is occupied by an electron and the high-energy one is empty. At positive $V = 0.49$ V, an electron can tunnel from the tip to the TMD (Fig. 4c, orange arrow), which is driven into a negatively charged (electron) resonance (ER). This state is only transiently populated as the TMD can be efficiently driven back to the GS by the tunnelling of extra electrons to/from the tip (substrate). The ES→GS relaxation process can happen either by direct tunnelling from HR (ER) to GS or by forming an exciton (ES) that subsequently recombines radiatively (red dashed arrow). The rightward/leftward orange (black) arrows represent electrons tunnelling to/from the MoSe$_2$ layer from/to the tip (substrate). The ES→GS radiative recombination rate is enhanced at the tip-sample plasmonic cavity by the Purcell effect (red halo). Note that relaxation through exciton formation is only possible for HR due to energy conservation.

### Conclusion and outlook

We have demonstrated STM-induced excitonic luminescence nanoscopy of an atomically resolved vdW heterostructure featuring...
short-period moiré superlattices. We directly reveal how the nanoscale environment influences the luminescence characteristics, leading to sizeable excitonic energy shifts and the emergence of emission from charged and localized excitons on areas separated only by a few nanometres. Previous studies on fluorescent dyes have demonstrated that STML with sub-molecular resolution can be achieved. Here, we have addressed an extended system, where the ESs are Wannier–Mott excitons that may diffuse over nano- to micrometer distances before recombining radiatively. Our measurements of localized excitons in spatially inhomogeneous areas (Fig. 2) reveal an upper bound of ~5 nm for the spatial resolution. Hyperspectral mapping of the STML signal provides a determination of the ultimate spatial resolution of our approach when applied to vdW heterostructures and will offer invaluable opportunities to explore exciton diffusion in the latter.

More broadly, STML offers exciting opportunities to unveil near-field charge and energy transfer and proximity effects in vdW heterostructures with unprecedented accuracy, offering outcomes in photonics, optoelectronics and nano-electronics. STML is also an ideal probe for correlated electronic phases and excitons in twisted-engineered heterostructures, starting with moiré-trapped interlayer excitons and trion formation in TMD heterobilayers, where the moiré period may approach 10 nm and hence may largely exceed the free-exciton Bohr radius. Finally, STML can be combined with tip-enhanced PL spectroscopy, possibly time resolved, to achieve a holistic picture of exciton physics in vdW materials at the atomic and sub-picosecond scales.

Online content
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the sample remained excited in the linear regime.

deviation over the noise level of each spectrum. (Fig. 4a) was acquired on a flat MoSe2 area at a constant height with a spectra (STS) on a clean Ag(111) surface. The tip quality is attested by a confocal microscopy setup. A linearly polarized continuous-wave at a temperature of 14 K in an optical cryostat coupled to a home-built vacuum (~10−5 mbar). The μPL response of our sample was studied in a vacuum, from the underlying Au substrate, and it simultaneously provides a smooth interface with MoSe2. In addition, the photophysics of MoSe2 coupled to mono- or few-layer graphene are largely similar, with only a slight increase in luminescence quenching as the number of graphene layers augments.

μPL characterization
The μPL response of our sample was studied in a vacuum (−10−5 mbar) at a temperature of 14 K in an optical cryostat coupled to a home-built confocal microscopy setup. A linearly polarized continuous-wave laser beam at a wavelength of 532 nm (2.33 eV) was used and the μPL signal was collected in the backscattering geometry and dispersed on a liquid-nitrogen-cooled charge-coupled device array using a 500 nm monochromator equipped with a grating with 150 grooves mm−1. To avoid thermal and mechanical drifts, hyperspectral PL mapping was performed using a short acquisition time per spectrum (1 s). A sufficiently high PL signal could be obtained using a moderate laser intensity of 30 μW μm−2 at the sample. In these conditions, we could verify that the sample remained excited in the linear regime.

STM and STML measurements
STM-based measurements were performed in a low-temperature (6 K) Unisoku STM operating in an ultrahigh vacuum and allowing optical measurements. The first lens (numerical aperture of 0.55), mounted on a three-axis piezo-controller, was used to collect and collimate the light emitted at the tip–sample junction. The emitted photons were redirected outside of the vacuum chamber through successive windows and viewports, and then refocused into an optical fibre connected to a monochromator coupled to a liquid-nitrogen-cooled charge-coupled device array, as done for the μPL measurements. Three different gratings were used, yielding spectral resolutions ranging from 0.60 down to 0.06 nm. Silver STM tips (prepared by preliminary indentations in a Ag(III) sample) were used to optimize the plasmonic response of the junction and enhance the radiative recombination rate at the tip–sample junction. To evaluate the quality, we recorded the dl/dV spectra (STS) on a clean Ag(III) surface. The tip quality is attested by a visible Ag(III) surface state in the STS measurement. The STS spectrum (Fig. 4a) was acquired on a flat MoSe2 area at a constant height with a current setpoint of I = 30 pA and a modulation voltage Vmod = 20 mV. The error bars in the STML data (Fig. 4a) correspond to one standard deviation over the noise level of each spectrum.

Data analysis
All the μPL and STML spectra presented in this work present both raw (light grey line) and smoothed (solid coloured line) data. Unless specified in the text, all the spectra were fit using Voigt profiles.

Reporting summary
Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability
Source data necessary to reproduce the results shown in the Article and Supplementary Information are available via figshare at https://doi.org/10.6084/m9.figshare.21913017. Additional data are available from the corresponding authors upon reasonable request. Source data are provided with this paper.

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Author contributions
S.B. and G.S. initiated and supervised the project. L.E.P.L., A.R., F.S. and G.S. built the STML setup. L.E.P.L. fabricated the sample and performed all the PL and STML measurements, with input from A.R., S.B. and G.S. L.E.P.L., S.B. and G.S. analysed the experimental data. All the authors discussed the results and contributed to the editing of the paper.

Competing interests
The authors declare no competing interests.

Additional information
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Reporting Summary

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Our web collection on statistics for biologists contains articles on many of the points above.

### Software and code

Policy information about availability of computer code

**Data collection**

Far-field optical measurements were performed using custom built optical setups and in particular a Cryo Industries of America continuous flow optical cryostat. STM studies were performed using a commercial UNISOKU system with optical access and a Nanonis control electronics. Princeton Instruments CCD cameras (Pylon and SPEC 10) and monochromators were used for all measurements of luminescence (photoluminescence and STM-induced luminescence). Our setups were controlled using custom made graphical user interfaces, either using Labview (version 10) or Python version 2.

**Data analysis**

The data were analysed using custom made Matlab (R2020) routines together with the origin pro software (version 2019).

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|----------------------------|-----|
| Population characteristics | n/a |
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