Fractionalization is a phenomenon in which strong interactions in a quantum system drive the emergence of excitations with quantum numbers that are absent in the building blocks. Outstanding examples are excitations with charge e/3 in the fractional quantum Hall effect1–2, solitons in one-dimensional conducting polymers3–4 and Majorana states in topological superconductors5. Fractionalization is also predicted to manifest itself in low-dimensional quantum magnets, such as one-dimensional antiferromagnetic S = 1 chains. The fundamental features of this system are gapped excitations in the bulk6 and, remarkably, S = 1/2 edge states at the chain termini7–9, leading to a four-fold degenerate ground state that reflects the underlying symmetry-protected topological order10,11. Here, we use on-surface synthesis12 to fabricate one-dimensional spin chains that contain the S = 1 poly cyclic aromatic hydrocarbon triangulene as the building block. Using scanning tunnelling microscopy and spectroscopy at 4.5 K, we probe length-dependent magnetic excitations at the atomic scale in both open-ended and cyclic spin chains, and directly observe gapped spin excitations and fractional edge states therein. Exact diagonalization calculations provide conclusive evidence that the spin chains are described by the S = 1 bilinear-biquadratic Hamiltonian in the Haldane symmetry-protected topological phase. Our results open a bottom-up approach to study strongly correlated phases in purely organic materials, with the potential for the realization of measurement-based quantum computation13.
On-surface synthesis of triangulene spin chains

Here, we use on-surface synthesis under ultra-high vacuum conditions to fabricate one-dimensional (1D) spin chains on a Au(111) surface, where the elementary building block is triangulene—a diradical polycyclic aromatic hydrocarbon (hereafter, nanographene) with $S = 1$ ground state (Fig. 1a). Magnetism in triangulene arises due to an inherent sublattice imbalance in its bipartite honeycomb lattice, which translates to a net spin imbalance\(^{22,23}\). Triangulene and its homologues, although challenging to synthesize by solution chemical routes\(^{24-26}\), have recently been synthesized on a range of metal and insulator surfaces\(^{27-30}\), and are shown to retain their magnetic ground states on the relatively inert Au(111) surface. We have previously shown that triangulene dimers, which consist of two triangulene units connected by a single carbon–carbon bond through their minority sublattice atoms, exhibit a large intertriangulene antiferromagnetic exchange of 14 meV (ref. 31). Furthermore, magnetic anisotropy in such carbon-based nanostructures is expected to be extremely weak\(^{32}\) (see Supplementary Note 1 for an estimation of the effect of extrinsic spin–orbit coupling on triangulenes). Therefore, we expect triangulene spin chains (TSCs) to provide an ideal platform to explore the spin physics of $S = 1$ chains.

The fabrication of TSCs relies on the solution synthesis of dimethylphenyl-substituted anthracene precursors 1 and 2 (Fig. 1b, see Supplementary Information for solution synthesis and characterization data), which undergo surface-catalysed Ullmann-like polymerization and subsequent oxidative cyclization upon thermal annealing on Au(111), thereby yielding the TSCs. We note that the use of only the dibrominated precursor 2 results in the growth of long TSCs with maximum length in excess of 100 nm (Supplementary Fig. 1). Therefore, we use a mixture of 2 and the monobrominated precursor 1 to limit the chain growth, resulting in short open-ended TSCs (oTSCs) with varying lengths, as shown in the overview STM image in Fig. 1c, which allows us to investigate the length-dependent magnetic structure of
TSCs. As shown in the bond-resolved STM images in Fig. 1d, e, TSCs with both cis and trans intertriangulene bonding configurations are found, with long chains mostly containing a mixed cis/trans structure. Scanning tunnelling spectroscopy (STS) measurements on TSCs over a wide bias range reveal an electronic bandgap of 1.60 eV irrespective of the cis/trans structure (Extended Data Fig. 1 and Supplementary Fig. 2). Our STS results are in agreement with spin-polarized density functional theory (DFT) calculations, which show an antiferromagnetic exchange between nearest-neighbour triangulene units, and nearly dispersionless frontier bands indicative of a weak intertriangulene electronic hybridization (Extended Data Fig. 2). We also performed many-body perturbation theory GW calculations on TSCs (where G and W denote Green’s function and screened Coulomb potential, respectively), including screening effects from the underlying surface, from which we obtain a theoretical electronic band gap of 1.43 eV that is consistent with the experimental bandgap.

**Magnetic excitations in triangulene spin chains**

Figure 1f, g presents high-resolution STM images of N = 16 oTSC (Fig. 1f) and cyclic TSC (cTSC, Fig. 1g) (where N denotes the number of triangulene units in a TSC). dV/dI spectroscopy (where I and V correspond to the tunnelling current and bias voltage, respectively) performed on these TSCs in the low-bias regime (|V| ≤ 100 mV; Fig. 1h, i) reveals two salient features. First, terminal units in the oTSC show peaks at zero bias (Fig. 1h), which exhibit an anomalous linewidth broadening with increasing temperature that is characteristic of a Kondo resonance33 (Supplementary Figs. 3–5). These Kondo resonances are absent both in the non-terminal units of the oTSC and throughout the cTSC (Fig. 1i) and, as is shown later, they are indicative of the emergence of S = 1/2 edge states. Second, several conductance steps symmetric with respect to zero bias and with energies below 50 meV are found throughout the oTSC and cTSC, corresponding to inelastic excitations. We ascribe these inelastic spectral features to spin excitations44–46 in the TSCs, as has been previously observed in spin chains of magnetic adatoms on surfaces47. The spin excitation energies, which reflect the energy difference between the magnetic ground state and the excited states, show a marked dependence on both N and the open-ended/cyclic topology of the TSCs. In addition, the spin excitation amplitudes exhibit a unit-to-unit modulation across a TSC that is linked to the spin spectral weight48 (see Methods), which is the probability of exciting the final state by means of spin-dependent electron tunnelling across a given location.

**Theoretical description**

A natural starting point to account for our experimental observations is the 1D Heisenberg model, \( \hat{H}_{\text{Heisenberg}} = \sum_i J \hat{S}_i \hat{S}_{i+1} \) (here, \( \hat{S}_i \) denotes the spin-1 operator at site \( i \) and \( J > 0 \) the exchange coupling), where individual triangulene units are described as \( S = 1 \) spins with a nearest-neighbour antiferromagnetic exchange. However, the Heisenberg model, with \( J \) taken to be 14 meV from STS measurements on an
that includes both bilinear and biquadratic exchange terms, and is referred to as the bilinear-biquadratic (BLBQ) model (here, $\beta$ is a parameter that determines the strength of the biquadratic term relative to the bilinear term). From a comparison of the BLBQ and Hubbard model calculations for an $N = 2$ TSC, we obtain $J = 18 \text{ meV}$ and $\beta = 0.09$, which, hereafter, we adopt for all values of $N$. The emerging physical picture is that cTSCs have a unique $S = 0$ ground state, which is qualitatively similar to the analytical solution obtained for $\beta = 1/3$—the Affleck–Kenney–Lieb–Tasaki (AKLT) limit—whose ground state is the valence bond solid given by the concatenation of singlets formed between two $S = 1/2$ virtual spins located at adjacent triangulene units (Fig. 2a). For oTSCs, the valence bond solid picture naturally accounts for the

$$H_{BLBQ} = \sum_i \left[ J \right] + \beta \left[ \mathbf{S}_i \cdot \mathbf{S}_i + \beta \left( \mathbf{S}_i \cdot \mathbf{S}_{i+1} \right)^2 \right]$$

Fig. 3 | Magnetic excitations in selected open-ended triangulene spin chains and comparison with the bilinear-biquadratic model. a–f, $\frac{d}{dV}$ spectroscopy on oTSCs with $N = 2$–6 and 9 (black curves). Representative bond-resolved STM images of oTSCs with $N = 2$–6 are shown (open feedback parameters: $V = 5 \text{ mV}, I = 50 \text{ pA}; \Delta h = 0.6$ or $0.7 \text{ Å}$). Also shown are the unit-resolved fits to the $\frac{d}{dV}$ spectra between $\pm 50 \text{ mV}$, obtained with the BLBQ model (orange curves; $J = 18 \text{ meV}, \beta = 0.09$ and effective temperature $T_{eff} = 5 \text{ K}$). Since the BLBQ model does not account for the underlying surface, it does not capture the Kondo exchange phenomena. Therefore, for the terminal units of $N = 3$ and 9 oTSCs, no fits are performed near the Kondo resonances. Coloured filled circles indicate the unique spin excitations experimentally observed for each $N$ ($N = 2$: 14 mV; $N = 3$: 0, 11 and 35 mV; $N = 4$: 6 and 37 mV; $N = 5$: 5, 25, 30 and 40 mV; $N = 6$: 6, 27 and 40 mV; $N = 9$: 0, 18, 28, 30, 36 and 40 mV). Open feedback parameters for the $\frac{d}{dV}$ spectra: $V = 100 \text{ mV}, I = 600 \text{ pA}$ (a) and $I = 1.4 \text{ nA}$ (b–f); $V_{rms} = 1 \text{ mV}$.
existence of fractional edge states with $S = 1/2$, which can be Kondo screened on a metal surface, and gapped bulk excitations. Since the terminal $S = 1$ units in an oTSC only have a single neighbour, one of their constituent $S = 1/2$ spins is excluded from the valence bond solid, thus generating unpaired spins (Fig. 2a). An effective interedge exchange couples these unpaired spins, leading to a singlet–triplet splitting whose magnitude decays exponentially with increasing $N$. In contrast, complete pairing of spins is achieved in a cTSC, and therefore no edge states are to be expected.

In addition to the low-energy edge excitations for oTSCs, the BLBQ model features multiple spin excitations at higher energies for both oTSCs and cTSCs. Some of them are spin waves spread across the entire TSC, while others are spin waves hybridized with the edge states (Extended Data Fig. 5). In Fig. 2b, we present the BLBQ spin excitation energies of oTSCs with $N = 2$–16, calculated with ED, where the size of the symbols accounts for the spin spectral weight of the corresponding spin excitation, with a larger weight leading to a more prominent step amplitude in $dV/dI$ spectroscopy. Our calculations show that (1) the edge excitation energy exponentially decreases with increasing $N$, and (2) the lowest energy bulk excitation extrapolates toward the Haldane gap with increasing $N$, in agreement with the experimental results (Extended Data Fig. 6). Figure 2c, d shows the average magnetization (Fig. 2c) and the spin spectral weight (Fig. 2d) of the edge state with the quantum numbers $|S, S_z| = |1, +1|$ for an $N = 16$ oTSC, revealing a strong localization of this state at the terminal triangulene units.

### Length-dependent magnetic excitations

We performed a systematic experimental study of spin excitations in seventeen oTSCs with $N$ between 2 and 20 (Fig. 3 and Supplementary Figs. 6–17), and eight cTSCs with $N = 5, 6, 12, 13, 14, 15, 16$ and 47 (Fig. 4 and Supplementary Figs. 18–23) that validate our theoretical picture. Figure 3 shows $dV/dI$ spectroscopy performed on oTSCs with $N = 2$–6 (Fig. 3a–e) and 9 (Fig. 3f), which reveals three principal features. First, all TSCs exhibit multiple spin excitations, with the exception of the $N = 2$ TSC, which shows a single (singlet–triplet) spin excitation at 14 meV. It is notable that the BLBQ model accurately accounts for both the energies and amplitude modulation of the spin excitation steps across the triangulene units for these chain lengths. The spin excitation energies calculated by ED of the BLBQ model for TSCs with $N ≥ 16$ exhibit a good agreement with the corresponding experimental spin excitation energies (Extended Data Fig. 6). Deviations between theory and experiments can be partially accounted for by the renormalization of excitation energies due to interactions with the metal surface and the extended metal chain.

Second, with the exception of the $N = 3$ TSC, the energy of the lowest energy spin excitation progressively decreases with increasing $N$, as predicted by the BLBQ model (Fig. 2b). Third, TSCs with $N ≥ 9$ exhibit Kondo resonances at the terminal units, which are a hallmark of topological degeneracy and fractionalization—Kondo resonances arise at the edges due to screening of the emergent $S = 1/2$ edge states by the underlying metal surface. The Kondo exchange competes with the interedge magnetic exchange, whose magnitude decays exponentially with increasing $N$, but overcomes the Kondo exchange for a small enough $N$ (experimentally, for $N ≤ 8$).

We note that the zero-bias resonances observed at the terminal units of the $N = 3$ TSC do not correspond to the emergent $S = 1/2$ edge states, given that $N$ is smaller than the spin correlation length $\xi = 4$ (Fig. 2b). It is observed that the amplitude of the zero-bias resonance for the $N = 3$ TSC is considerably lower than that of the Kondo excitations for oTSCs with $N ≥ 9$. We calculated the spectral function for the $N = 3$ TSC with a non-perturbative treatment of a multi-orbital Anderson model (MOAM), including coupling to the surface (see Methods and Extended Data Fig. 7). These calculations show that the zero-bias resonance in the $N = 3$ TSC can be associated to a Kondo resonance of an $S = 1$ ground state, in agreement with previous works. Our calculations also account for the spin excitation steps that are experimentally observed for the $N = 3$ oTSC. Given the large computational cost of such calculations, we presently cannot employ them for TSCs with $N > 3$.

A final confirmation of the validity of the BLBQ model to describe TSCs comes from STS measurements on cTSCs. Figure 4a, b shows high-resolution STM images of $N = 6$ and 13 cTSCs. $dV/dI$ spectroscopy on these cTSCs (Fig. 4c–e) reveals spin excitations that are in agreement with the prediction of the BLBQ model using the same parameters as for the oTSCs. Expectedly, no Kondo resonances are observed in cTSCs given the absence of terminal units. Moreover, the spin excitation spectra for all units of a cTSC are roughly identical, reflecting the equivalence of units in a cyclic structure.
**Outlook**

The ground state of the BLBQ model in the AKLT limit, as well as its generalization in two dimensions, are known to be a resource for universal measurement-based quantum computation. Our results should therefore motivate future work addressing the possibility to tune $\beta$, so that these non-trivial quantum states naturally occur as the ground state of coupled magnetic nanographenes. On a general note, our on-surface synthetic protocol demonstrated here for TSCs can be extended to afford scalable fabrication of purely organic quantum spin chains, two-dimensional lattices and networks—thus opening exciting opportunities in the realization of non-trivial spin liquid phases, quantum simulators and nanoscale spintronic devices.

**Note added in proof:** We have become aware of a related work on synthesis and characterization of a triangulene macrocycle.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability https://doi.org/10.1038/s41586-021-03842-3.
Methods

Sample preparation and STM/STS measurements
STM measurements were performed with a low-temperature STM from Scienta Omicron operating at a temperature of 4.5 K and base pressure below $5 \times 10^{-10}$ mbar. Au(111) single-crystal surfaces were prepared through cycles of Ar$^+$ sputtering and subsequent annealing at 723 K. Powder samples of precursors 1 and 2 were contained in quartz crucibles and sublimed from a home-built evaporator at 323 K and 343 K, respectively, onto Au(111) surface held at room temperature. STM images and $\partial I/\partial V$ maps were recorded either in constant-current or constant-height modes, while $\partial I/\partial V$ spectra were recorded in constant-height mode. For constant-height STM imaging and $\partial I/\partial V$ mapping, feedback was opened above the TSC. Bias voltages are provided with respect to the sample. All $\partial I/\partial V$ measurements were obtained using a lock-in amplifier (SR830, Stanford Research Systems) operating at a frequency of 860 Hz. Modulation voltages for each measurement are reported as root mean squared amplitude ($V_{\text{rms}}$). $\partial I/\partial V$ spectra were obtained by numerical differentiation of the corresponding $\partial I/\partial V$ curves, with a binomial smoothing (1–5 iterations) applied to the $\partial I/\partial V$ curves. Unless otherwise noted, STM and STS measurements were performed with gold-coated tungsten tips. Bond-resolved STM images were acquired by scanning the TSCs with CO functionalized tips in constant-height mode. CO molecules were deposited onto a cold sample (with a maximum sample temperature of 13 K) containing the reaction products. Analysis of Kondo resonances was performed following the procedure in ref. 13. The data reported in this study were processed with WaveMetrics Igor Pro software.

DFT and GW calculations
DFT band structure calculations of TSCs were performed in the gas-phase with the Quantum Espresso$^{13}$ software package using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional$^{44}$. A plane wave basis with an energy cut-off of 400 Ry for the charge density was used together with the projector augmented-wave method (PAW) pseudo-potentials (standard solid-state pseudo potentials (SSSP)$^{45}$). Monkhorst–Kresse meshes of $12 \times 1 \times 1$ and $10 \times 1 \times 1$ were used for TSCs with two (trans TSC) and four (cis TSC) triangulene units in the periodic cell, respectively. The cell and atomic geometries were relaxed until forces were smaller than 0.001 a.u.

The adsorption geometry of an $N = 6$ oTSC on Au(111) was calculated with the CP2K$^{46}$ software package using the PBE exchange-correlation functional together with the DFT-D3 van der Waals scheme proposed by Grimme et al.$^{50}$, and norm-conserving Goedecker–Teter–Hutter (GTH) pseudo-potentials$^{48}$. A TZVP MOLOPT basis set$^{46}$ was used for C and H species, and a DZVP MOLOPT basis set for the Au species, together with a cut-off of 600 Ry for the plane wave basis set. An unrestricted Kohn–Sham approach was used for the TSCs together with an antiferromagnetic spin guess to model the magnetic ground state. The surface/adsorbate system was modelled within the repeated slab scheme, with a simulation cell containing four atomic layers of Au along the [111] direction and a layer of hydrogen atoms to suppress one of the two Au(111) surface states. 40 Å of vacuum was included in the simulation cell to decouple the system from its periodic replicas in the direction perpendicular to the surface. The gold surface was modelled by a supercell of $67.80 \times 35.74$ Å corresponding to 322 surface units. The adsorption geometry was optimized by keeping the positions of the bottom two layers of the slab fixed to the ideal bulk coordinates, while all the other atoms were relaxed until forces were lower than 0.005 eV Å$^{-1}$.

The eigenvalue self-consistent GW calculations$^{49}$ were performed with the CP2K code on a trans $N = 6$ oTSC in the gas-phase, with the geometry corresponding to the adsorption configuration of the TSC on Au(111). The calculations were performed based on the unrestricted DFT PBE wavefunctions using the GTH pseudo-potentials and analytic continuation with a two-pole model. The aug-DZVP basis set from Wilhelm et al.$^{50}$ was used. To account for screening by the Au(111) surface, we applied the image charge model by Neaton et al.$^{51}$, and to determine the image plane position with respect to the molecular geometry, we used a distance of 1.42 Å between the image plane and the first surface layer, as reported by Kharche and colleagues$^{52}$.

The calculations were performed using the AiiDA lab platform$^{53}$.

Derivation of the BLBQ model
Our starting point to describe the TSCs is a tight-binding model where we only consider $p_\sigma$ orbitals from carbon$^{23,54}$, which we refer to as the complete tight-binding model. The resulting single-particle spectrum for a TSC with $N$ triangulenes features 2N zero-energy states, each hosting one electron, which arise due to the inherent sublattice imbalance in triangulene. Strict zero-energy states occur within the nearest-neighbour tight-binding approximation, whereas the presence of third-nearest-neighbour hopping leads to hybridization of the zero-energy states. To describe the formation of local magnetic moments and their exchange interaction, we include electron–electron interactions in the Hubbard approximation, where only intra-atomic Coulomb repulsion ($U > 0$) is considered. Comparison of the Hubbard model with DFT calculations justifies this approximation$^{31,54}$. Furthermore, we employ the CAS approximation, where we consider a subset of many-body states: the occupation of the set of molecular orbitals that correspond to the 2N hybridized zero-energy states is allowed to vary, whereas the occupation of orbitals lower or higher in energy is frozen. The Hubbard model is represented in this restricted space and diagonalized numerically. The CAS approximation for a single triangulene and an $N = 2$ TSC predicts $S = 1$ and $S = 0$ ground states, respectively$^{23,54}$. The CAS approximation allows us to obtain the spin excitation energies as a function of $U$ for oTSCs with $N \leq 4$ ($t_1 = -2.70$ eV, $t_2 = 0$ eV and $t_3 = -0.35$ eV; where $t_1$, $t_2$, and $t_3$ denote the first-, second- and third-nearest-neighbour hopping parameters, respectively$^{54}$). By comparing the calculated spin excitation energies with the corresponding experimental values (Extended Data Fig. 3), we infer $U > 2t_1$.

To address oTSCs with $N > 4$, which are beyond our current computational capabilities using the CAS approximation, we instead use a simpler tight-binding toy model that captures the salient features of triangulene, that is (1) $C_2$ symmetry and (2) a sublattice imbalance of two, resulting in two zero-energy states$^{54}$. We refer to this model as the four-site model. This model has two parameters $t_1$ and $t_2$ that describe intratriangulene and intertriangulene hopping, respectively, along a TSC (Extended Data Fig. 3). We choose $t_1 = -1.11$ eV and $t_2 = -0.20$ eV, such that the low-energy single-particle spectra of both the complete and the four-site tight-binding models are the same for arbitrary chain lengths. Importantly, comparison of the low-energy many-body spectra of an $N = 3$ oTSC for both the complete and the four-site Hubbard models, as a function of $U$, validates this approach (Extended Data Fig. 3).

We can model oTSCs with $N \leq 6$, described with the four-site model, using DMRG as implemented in the iTensor$^{24}$ library. For a fixed $U = 1.45$ (i), DMRG calculations are in agreement with both the CAS approximation and experiments (Extended Data Fig. 3). Importantly, for oTSCs with $N = 2$–6, the DMRG calculations match not only the experimental spin excitation energies, but also the unit-to-unit modulation of the spin excitation amplitudes (Extended Data Fig. 4).

Given the large ferromagnetic exchange coupling within each triangulene unit, together with the report of an antiferromagnetic exchange coupling between neighbouring triangulene units$^{31}$ and the expectation of an extremely weak magnetic anisotropy$^{55}$, it would be natural to expect that TSCs may be described by the 1D antiferromagnetic $S = 1$ Heisenberg model. However, despite capturing the modulation of the spin excitation amplitudes, the Heisenberg model fails to provide a quantitative agreement of the spin excitation energies with both the experiments and Hubbard model calculations (Extended Data Fig. 3), which implies that some correction must be lacking. The inclusion of exchange terms beyond nearest-neighbour exchange was disregarded due to two reasons. First, in the case of an $N = 2$ TSC, where...
such corrections are obviously zero (since an \( N = 2 \) TSC consists of nearest-neighbour triangulene units only), we already find considerable disagreement of the Heisenberg model with Hubbard model calculations (Extended Data Fig. 3). Second, for an \( N = 3 \) oTSC, we have verified that adding a second-nearest-neighbour exchange term does not lead to an overall better agreement (Supplementary Note 2 and Supplementary Fig. 24). As a consequence, we have considered corrections in the form of a nearest-neighbour biquadratic exchange term, which is the simplest term compatible with all the previous arguments. The resulting Hamiltonian is the so-called BLBQ model.

The excitation energies computed with the Hubbard model, both for the four-site and complete versions, can be compared with those of the BLBQ model to derive the parameters \( J \) and \( \beta \). Specifically, using the four-site Hubbard model results for the \( N = 2 \) TSC, we determine \( J = 18 \) meV and \( \beta = 0.09 \) (Extended Data Fig. 3). We then extend the comparison of the four-site Hubbard and BLBQ models for oTSCs with \( N = 3 \), 6, while using the aforementioned values of \( J \) and \( \beta \). We find that the calculated spin excitation energies exhibit an excellent match, with differences smaller than 3 meV. Additionally, we obtain the same pattern of spin degeneracies and identical spin spectral weights (Extended Data Fig. 4) using both models.

Finally, using ED of the BLBQ model, with the help of the QuSpin package\(^{62-64} \), we could extend our calculations for both oTSCs and cTSCs with \( N \leq 16 \). Comparison with the experimental data (Figs. 3 and 4) provides the final evidence that the BLBQ model describes the TSCs.

Modelling of low-bias experimental \( dI/dV \) spectra

The calculated \( dI/dV \) spectra in the main text are obtained using the following expression, which treats coupling to the substrate to the lowest order\(^{60} \):

\[
\frac{dI}{dV} \mid _n = g_0 \sum_M \sum_{M',a=x,y,z} |\langle MS_M(n)|M'\rangle|^2 \Theta_M(eV)
\]  

(2)

where \( n \) denotes the triangulene unit on which the \( dI/dV \) spectrum is recorded, \( M \) and \( M' \) denote the many-body states of triangulene, \( g_0 \) is a constant prefactor, \( \Theta_M(eV) \) is the thermally broadened step function centred around \( eV = (E_M - E_0) \) (\( e \) is the elementary charge), where \( E_M - E_0 \) is the excitation energy for a transition from state \( M \) to \( M' \), and \( S_M(n) \) is the \( S = 1 \) spin operators acting on the \( n \)th triangulene unit. The expression for \( dI/dV \) contains the spin spectral weight, defined for the state \( M' \) and the \( n \)th triangulene unit as

\[
S_M(n) = \sum_M \sum_{a=x,y,z} |\langle MS_M(n)|M'\rangle|^2
\]  

(3)

Equation (2) relates the \( dI/dV \) spectra to the many-body wavefunctions and excitation energies. Specifically, it yields stepwise \( dI/dV \) curves, with steps at \( eV = \pm (E_M - E_0) \) and relative heights determined by the spin spectral weights. Importantly, for a given pair of states \( M \) and \( M' \), the height of the inelastic step can change for different triangulene units \( n \). Thus, the theory predicts both the energies of the inelastic \( dI/dV \) steps and the modulation of their heights across a TSC.

The matrix elements in \( S_M(n) \) are only non-zero for states \( M \) and \( M' \) whose total spin quantum number \( S \) differ by zero or one, reflecting the conservation of the total spin of the system formed by the tunneling electron and triangulene. In addition, equation (2) contains the following sum rule for spin-1 models: for very large \( eV \), the unit-resolved \( dI/dV \) saturates to \( 8S(S+1)g_0^2 = 2g_0^2 \). We have verified that by considering transition energies up to 50 meV, we have, for all TSCs described by the BLBQ model, more than 92% of the spin spectral weight in each unit, and more than 96% of the total spin spectral weight (that is, the spin spectral weight summed over all units).

To compare the experimental \( dI/dV \) spectra, which is in arbitrary units, to the theoretical predictions given by equation (2), we make a fit to set the constant of proportionality \( g_0 \) (we also allow for a vertical shift that has no physical relevance). For cTSCs, where all the triangulene units are equivalent, we average the experimental \( dI/dV \) spectra of all the units, and we perform a single fit. In the case of oTSCs, variations of the heights of the spin excitation steps are expected across different units\(^{23,60} \), so that we perform one fit for each experimental curve, using the expression \( m(n) \times \frac{dI}{dV}(n) + b(n) \), where \( m \) and \( b \) are fitting parameters. This fit assumes that the constant of proportionality may change when the tip is moved laterally to scan across the nanostructure, which can occur due to surface variations or minor vertical tip deviations. It must be noted that these fitting parameters do not change the relative height of the steps in \( dI/dV \). Thus, only the spin spectral weight matrix elements control the relative heights in a given unit.

For the \( N = 3 \) oTSC, we have also calculated the \( dI/dV \) spectra, including the coupling to the surface, non-perturbatively for a MOAM formed by the zero-energy states of triangulene. The \( dI/dV \) spectra are calculated as the spectral function of the zero-energy states in the non-crossing approximation (NCA), which is capable of modelling Kondo resonances. However, the computational cost of these calculations is too high for \( N > 3 \).

The starting point for the MOAM-NCA calculations is the complete Hubbard model, with twenty-two states per triangulene, for an \( N = 3 \) oTSC, taking into account nearest-neighbour and third-nearest-neighbour hopping \( t_1 = -2.70 \) eV, \( t_2 = 0 \) eV, \( t_3 = -0.35 \) eV and \( U = 1.90|t_1| \). The occupation of the carbon sites is controlled by the on-site energy \( \varepsilon \). An on-site energy of \( \varepsilon = -0.47 \) eV ensures both charge neutrality and particle-hole symmetry. Deviation from the particle–hole symmetry point is measured by \( \delta \varepsilon = \varepsilon - \varepsilon^\prime \). With \( \delta \varepsilon = 0 \), the single-particle spectrum would have six zero-energy states, \( t_1 \) partially lifts this degeneracy, leaving two zero-energy states and four low-energy states, all well separated from the other molecular levels. These six single-particle states, which we label with index \( k \), form the localized states of the MOAM. We assume the single-particle broadening (hybridization) \( \Gamma \) to the bath to be equal for all local levels and energy independent. In addition, finite values of \( \delta \varepsilon \) allow charge fluctuations and lift particle–hole symmetry (Extended Data Fig. 7).

In order to solve the MOAM, NCA expands the eigenstates of the isolated impurity in the coupling \( \mathcal{I} \) to the bath\(^{45} \). The first step is thus an exact diagonalization of the impurity Hamiltonian. The eigenstates are simultaneously eigenstates of the total number of electrons \( N_e \) and the total spin. At half-filling (\( N_e = 6 \)), the ground state is an \( S = 1 \) spin triplet, and the first and second excited states are \( S = 0 \) and \( S = 2 \), respectively. Coupling to the surface leads to fluctuations of electrons in the impurity, and thus requires the charged sectors with \( N_e \pm 1 \) electrons. The solution yields the orbital-resolved spectral function \( A_{\mathcal{I}}(\omega) \) from which the atom-resolved spectral function \( A_{\mathcal{I}}(\omega) \) can be calculated, which is proportional to \( dI/dV \) (refs. \(^{62-64} \)). More details on the application of the NCA to nanoscale quantum magnets can be found in ref. \(^{44} \).

Synthesis of molecular precursors

The synthesis of molecular precursors\(^1 \) and \(^2 \), and associated characterization data, are reported in Supplementary Figs. 25–49.

Data availability

The data that support the findings of this study are available at the Materials Cloud platform (https://doi.org/10.24435/materialscloud:e8-aq).

Code availability

The custom-designed Python codes that were used for solving the bilinear-biquadratic spin Hamiltonian by exact diagonalization are available on the GitHub repository (https://github.com/GCata-rina/ED_BLBQ). All other codes are available from J.F.R. (joaquin.fernandez-rossier@inl.int) upon reasonable request.
Extended Data Fig. 1 | Scanning tunnelling spectroscopy measurements of the frontier bands of triangulene spin chains. a, b, $dI/dV$ spectroscopy on TSCs with cis (a) and trans (b) intertriangulene bonding configurations (open feedback parameters: $V = -1.5\, \text{V}$, $I = 250\, \text{pA}$; $V_{\text{rms}} = 16\, \text{mV}$). Acquisition positions are marked with filled circles in c, d. Irrespective of the bonding configuration, TSCs exhibit an electronic band gap of 1.6 eV. c, d, High-resolution STM images (top panels), and constant-current $dI/dV$ maps of the valence (middle panels) and conduction (bottom panels) bands of cis (c) and trans (d) TSCs. Scanning parameters: $V = -0.4\, \text{V}$, $I = 250\, \text{pA}$ (top and middle panels, c, d) and $V = 1.1\, \text{V}$, $I = 280\, \text{pA}$ (bottom panels, c, d); $V_{\text{rms}} = 30\, \text{mV}$. All measurements were performed with a CO functionalized tip.
Extended Data Fig. 2 | Gas-phase density functional theory calculations on triangulene spin chains. 

a, e, DFT band structure and density of states (DOS) plots of TSCs with cis (a) and trans (e) intertriangulene bonding configurations in their antiferromagnetic ground state. Energies \( E \) are given with respect to the vacuum level. A Gaussian broadening of 100 meV has been applied to the DOS plots. Note that spin up and spin down bands are energetically degenerate. 

b, f, Corresponding band structure plots around the frontier bands. \( k \) denotes the reciprocal lattice vector. The unit cells for the band structure calculations contain four and two triangulene units for cis and trans TSCs, respectively, with the lattice periodicities \( a = 30.0 \, \text{Å} \) (cis TSC) and 17.4 Å (trans TSC). The dashed lines indicate the middle of the band gap. The calculations reveal nearly dispersionless frontier bands due to a weak intertriangulene electronic hybridization. In addition, TSCs exhibit a band gap of 0.68 eV irrespective of the intertriangulene bonding configuration. 

c, g, Ground state spin density distributions for cis (c) and trans (g) TSCs. Spin up and spin down densities are denoted in blue and red, respectively. 

d, h, Local DOS maps of the valence (VB) and conduction (CB) bands of cis (d) and trans (h) TSCs. Spin density distributions and local DOS maps were calculated at a height of 3 Å above the TSCs.
Extended Data Fig. 3 | Derivation of the bilinear-biquadratic model.

**a,** Schematic energy level diagram of $N = 2$ (a) and 3 (b) oTSCs for the Heisenberg, Hubbard and BLBQ models. Analytical expressions for the spin models are provided in the Supplementary Information (Supplementary Note 2). The Hubbard model is defined such that each triangulene unit is represented by a four-site lattice (c) and the many-body energy levels are computed with DMRG, taking $t = -1.11 \, \text{eV}$, $t' = -0.20 \, \text{eV}$ and $U = 1.45|t|$. The parameters of the BLBQ model ($J = 18 \, \text{meV}$ and $\beta = 0.09$) are obtained by matching its excitation energies to those of the Hubbard model for the $N = 2$ TSC. **c,** Description of the four-site toy model with the intra- and intertriangulene hopping, $t$ and $t'$, respectively, indicated. The coloured filled circles denote the two sublattices. **d,** Comparison of the excitation energies for an $N = 3$ oTSC computed with CAS(6,6) for the complete Hubbard model with $t_1 = -2.70 \, \text{eV}$, $t_2 = 0 \, \text{eV}$ and $t_3 = -0.35 \, \text{eV}$ (d), and with DMRG for the four-site Hubbard model (e), as the atomic Hubbard $U$ is varied. Dashed lines indicate the experimental spin excitation energies of 14 \, \text{meV} for $N = 2$ TSC (a) and 11 and 35 \, \text{meV} for $N = 3$ oTSC (b, d). Note that the Heisenberg model fails to capture both the experimental spin excitation energies for the $N = 3$ oTSC (b), and the Hubbard model results for the $N = 2$ TSC (a) and $N = 3$ (b) oTSCs.
Extended Data Fig. 4 | Experimental and theoretical spectroscopic signatures of spin excitations in an $N = 4$ open-ended triangulene spin chain. Comparison between experimental and theoretical (using the four-site Hubbard and BLBQ models) $d^2/dV^2$ spectra of an $N = 4$ oTSC shows a good agreement in both the energies and the modulation of the spin spectral weight across the different units in the TSC. Numerals along the abscissa denote the unit number of the TSC. BLBQ model calculations are performed with two different $T_{\text{eff}}$ values for the tunnelling quasiparticle, which determine the linewidth of the $d^2/dV^2$ profile. Model parameters are the same as in Extended Data Fig. 3.
Extended Data Fig. 5 | Average magnetization for the first three $S_z = +1$ states of an $N = 16$ open-ended triangulene spin chain, obtained with the bilinear-biquadratic model. Calculations were performed with $J = 18\,\text{meV}$ and $\beta = 0.09$. Orange filled circles denote the magnetization profile of the state with the lowest excitation energy $\mathcal{E} = 0.4\,\text{meV}$, much smaller than the theoretical Haldane gap (9 meV). The average magnetization is clearly the largest at the terminal units, and is strongly depleted at the central units, as expected for an edge state. Blue and green filled circles denote spin excitations with energies larger than the theoretical Haldane gap. Blue filled circles correspond to a state with $\mathcal{E} = 12.1\,\text{meV}$ and $|S, S_z = 1, +1\rangle$, where the magnetization profile forms a nodeless standing wave with maximum average magnetization at the central units. This can be identified as a spin wave state, except for the minor upturn at the terminal units. Green filled circles are associated to a state with $\mathcal{E} = 11.6\,\text{meV}$ and $|S, S_z = 2, +1\rangle$, where the average magnetization shares similarities with both the edge and nodeless spin wave states.
Extended Data Fig. 6 | Theoretical and experimental spin excitation energies of open-ended and cyclic triangulene spin chains. 

a, Spin excitation energies calculated by ED of the BLBQ model ($J = 18$ meV and $\beta = 0.09$) for oTSCs with $N = 2$–16 (circles) and cTSCs with $N = 5, 6, 12, 13, 14, 15$ and 16 (crosses) up to 50 meV. The size of the symbols accounts for the spin spectral weight of the corresponding spin excitation. The lowest energy bulk excitation, as indicated for the $N = 16$ cTSC, converges to the Haldane gap (9 meV) with increasing $N$. 

b, Experimental spin excitation energies up to 50 meV for seventeen oTSCs with $N$ between 2 and 20, and eight cTSCs with $N = 5, 6, 12, 13, 14, 15, 16$ and 47. The lowest energy bulk excitation, indicated for the $N = 47$ cTSC, converges to the Haldane gap (14 meV) with increasing $N$. Experimentally, starting from both $N = 16$ oTSC and cTSC, convergence to the Haldane gap is observed. Note the odd–even effect observed for the lowest energy excitation of cTSCs, seen both in theory and experiments.
Extended Data Fig. 7 | Non-crossing approximation results for the multi-orbital Anderson model of an $N = 3$ open-ended triangulene spin chain ($t_1 = -2.70$ eV, $t_2 = 0$ eV, $t_3 = -0.35$ eV and $U = 1.90|t_1|$) coupled to the surface ($J/\pi = 13$ meV). a, Total spectral function of CAS(6,6) at different temperatures $T$ for the case of particle–hole symmetry. b, Orbital-resolved spectral function of CAS(6,6) for $T = 4.64$ K and for the particle–hole symmetric case. c, Detuning from particle–hole symmetry: total spectral function of CAS(6,6) for different values of $\delta \epsilon$ and $T = 4.64$ K. d, Local spectral functions at $T = 4.64$ K for carbon sites of one of the outer triangulene units and the central triangulene unit ($\delta \epsilon = 200$ meV). The inset shows a sketch of the $N = 3$ oTSC with the two carbon sites marked with the corresponding coloured filled circles. The spectral functions in individual panels are offset vertically for visual clarity.