

## Postprint

This document is the Accepted Manuscript version of a Published Work that appeared in final form in  
after peer review and technical editing by the publisher.

To access the final edited and published work see:

Access to the published version may require subscription.

When citing this work, please cite the original published paper.

## 1 Observation of fractional edge excitations in nanographene spin chains

2  
3 Shantanu Mishra<sup>1,9\*</sup>, Gonçalo Catarina<sup>2,3\*</sup>, Fupeng Wu<sup>4</sup>, Ricardo Ortiz<sup>3</sup>, David Jacob<sup>5,6</sup>, Kristjan  
4 Eimre<sup>1</sup>, Ji Ma<sup>4</sup>, Carlo A. Pignedoli<sup>1</sup>, Xinliang Feng<sup>4,7,†</sup>, Pascal Ruffieux<sup>1,†</sup>, Joaquín Fernández-  
5 Rossier<sup>2,†</sup> and Roman Fasel<sup>1,8</sup>

6  
7 <sup>1</sup>Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

8 <sup>2</sup>International Iberian Nanotechnology Laboratory, Braga, Portugal

9 <sup>3</sup>University of Alicante, Sant Vicent del Raspeig, Spain

10 <sup>4</sup>Technical University of Dresden, Dresden, Germany

11 <sup>5</sup>University of the Basque Country, San Sebastián, Spain

12 <sup>6</sup>IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

13 <sup>7</sup>Max Planck Institute of Microstructure Physics, Halle, Germany

14 <sup>8</sup>University of Bern, Bern, Switzerland

15 <sup>9</sup>Present address: IBM Research – Zurich, Rüschlikon, Switzerland

16  
17 \*These authors contributed equally to this work.

18 †E-mail: xinliang.feng@tu-dresden.de; pascal.ruffieux@empa.ch; joaquin.fernandez-rossier@inl.int

19  
20 **Fractionalization is a phenomenon in which strong interactions in a quantum system drive**  
21 **the emergence of excitations with quantum numbers that are absent in the building blocks.**  
22 **Outstanding examples are excitations with charge  $e/3$  in the fractional quantum Hall**  
23 **effect<sup>1,2</sup>, solitons in one-dimensional conducting polymers<sup>3,4</sup> and Majorana states in**  
24 **topological superconductors<sup>5</sup>. Fractionalization is also predicted to manifest itself in low-**  
25 **dimensional quantum magnets, such as one-dimensional antiferromagnetic  $S = 1$  chains.**  
26 **The fundamental features of this system are gapped excitations in the bulk<sup>6</sup> and,**  
27 **remarkably,  $S = 1/2$  edge states at the chain termini<sup>7–9</sup>, leading to a four-fold degenerate**  
28 **ground state that reflects the underlying symmetry-protected topological order<sup>10,11</sup>. Here,**  
29 **we use on-surface synthesis<sup>12</sup> to fabricate one-dimensional spin chains that contain the  $S =$**   
30 **1 polycyclic aromatic hydrocarbon triangulene as the building block. Using scanning**  
31 **tunneling microscopy and spectroscopy at 4.5 K, we probe length-dependent magnetic**  
32 **excitations at the atomic scale in both open-ended and cyclic spin chains, and directly**  
33 **observe gapped spin excitations and fractional edge states therein. Exact diagonalization**  
34 **calculations provide conclusive evidence that the spin chains are described by the  $S = 1$**   
35 **bilinear-biquadratic Hamiltonian in the Haldane symmetry-protected topological phase.**  
36 **Our results open a bottom-up approach to study strongly correlated phases in purely**  
37 **organic materials, with the potential for the realization of measurement-based quantum**  
38 **computation<sup>13</sup>.**

39  
40 In one dimension, quantum fluctuations quench long-range magnetic order, enabling the  
41 emergence of exotic phenomena such as fractionalization. The notion that spin chains with an  
42 antiferromagnetic Heisenberg exchange lack a classical magnetic order, and have a gapless  
43 excitation spectrum with a continuum of excited states above the ground state, goes back to the  
44 early theoretical work of Bethe performed almost a century ago for  $S = 1/2$  chains<sup>14</sup> (where  $S$   
45 denotes the total spin quantum number of the elementary building block). In contrast to half-

integer spin chains, Haldane predicted that integer spin chains with periodic boundary conditions should have a gapped excitation spectrum between a singlet ground state and the first excited state<sup>6</sup>, known as the Haldane gap. It was later found that open-ended  $S = 1$  chains additionally host fractional  $S = 1/2$  edge states at the chain termini<sup>7-9</sup>. These edge states are coupled via an interedge effective exchange that gives rise to a singlet-triplet splitting, which decays exponentially with increasing chain length and results in a four-fold degeneracy of the ground state in the thermodynamic limit. The situation where the ground state degeneracy depends upon the open-ended or closed (cyclic) nature of the chains is a hallmark of topological order. In the case of  $S = 1$  chains, topological order is associated to symmetries such as  $SO(3)$ , time reversal and link inversion, and is known as symmetry-protected topological order<sup>10,11</sup>.

In the past three decades, a plethora of experimental work has explored the existence of the Haldane gap and fractional edge excitations in materials containing quasi-one-dimensional  $S = 1$  chains of transition metal ions<sup>15</sup>, employing ensemble probes such as neutron scattering, electron spin resonance and thermodynamic property measurements. However, magnetic anisotropy of transition metal ions and a finite interchain magnetic exchange, inherently present in these materials, are detrimental for the emergence of the Haldane phase. An alternative approach to achieve physical realization of spin chains relies on the ability to image and manipulate individual atoms or molecules on solid surfaces by the scanning tunneling microscope (STM). Combined with the ability of STM to measure local electronic structure<sup>16</sup> and magnetic excitations<sup>17</sup> at the atomic scale, recent years have witnessed on-demand fabrication of atomic spin chains and demonstration of complex magnetic interactions and topological phenomena therein<sup>18</sup>, including the realization of quantum  $S = 1/2$  models<sup>19,20</sup>. However, the Haldane phase has so far not been realized using this approach, despite predictions to such effect<sup>21</sup>.

### 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<sup>22,23</sup>. Triangulene and its homologues, although challenging to synthesize by solution chemical routes<sup>24-26</sup>, have recently been synthesized on a range of metal and insulator surfaces<sup>27-30</sup>, 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<sup>31</sup>. Furthermore, magnetic anisotropy in such carbon-based nanostructures is expected to be extremely weak<sup>32</sup> (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-catalyzed Ullmann-like polymerization and subsequent oxidative cyclization upon thermal annealing on Au(111), thereby yielding the TSCs.

89 We note that the use of only the dibrominated precursor **2** results in the growth of long TSCs with  
 90 maximum length in excess of 100 nm (Supplementary Fig. 1). Therefore, we use a mixture of **2** and  
 91 the monobrominated precursor **1** to limit the chain growth, resulting in short open-ended TSCs  
 92 (oTSCs) with varying lengths, as shown in the overview STM image in Fig. 1c, which allows us to  
 93 investigate the length-dependent magnetic structure of TSCs. As shown in the bond-resolved STM  
 94 images in Fig. 1d,e, TSCs with both *cis* and *trans* intertriangulene bonding configurations are found,  
 95 with long chains mostly containing a mixed *cis/trans* structure. Scanning tunneling spectroscopy  
 96 (STS) measurements on TSCs over a wide bias range reveal an electronic band gap of 1.60 eV  
 97 irrespective of the *cis/trans* structure (Extended Data Fig. 1 and Supplementary Fig. 2). Our STS  
 98 results are in agreement with spin-polarized density functional theory (DFT) calculations, which  
 99 show an antiferromagnetic exchange between nearest-neighbor triangulene units, and nearly  
 100 dispersionless frontier bands indicative of a weak intertriangulene electronic hybridization  
 101 (Extended Data Fig. 2). We also performed many-body perturbation theory  $GW$  calculations on  
 102 TSCs (where  $G$  and  $W$  denote Green's function and screened Coulomb potential, respectively),  
 103 including screening effects from the underlying surface, from which we obtain a theoretical  
 104 electronic band gap of 1.43 eV that is consistent with the experimental band gap.

105

### 106 **Magnetic excitations in open-ended and cyclic spin chains**

107 Figure 1f,g presents high-resolution STM images of  $N = 16$  oTSC (Fig. 1f) and cyclic TSC  
 108 (cTSC, Fig. 1g) (where  $N$  denotes the number of triangulene units in a TSC).  $dI/dV$  spectroscopy  
 109 (where  $I$  and  $V$  correspond to the tunneling current and bias voltage, respectively) performed on  
 110 these TSCs in the low-bias regime ( $|V| \leq 100$  mV; Fig. 1h,i) reveals two salient features. First,  
 111 terminal units in the oTSC show peaks at zero bias (Fig. 1h), which exhibit an anomalous linewidth  
 112 broadening with increasing temperature that is characteristic of a Kondo resonance<sup>33</sup>  
 113 (Supplementary Figs. 3–5). These Kondo resonances are absent both in the non-terminal units of  
 114 the oTSC and throughout the cTSC (Fig. 1i) and, as is shown later, they are indicative of the  
 115 emergence of  $S = 1/2$  edge states. Second, several conductance steps symmetric with respect to  
 116 zero bias and with energies below 50 meV are found throughout the oTSC and cTSC,  
 117 corresponding to inelastic excitations. We ascribe these inelastic spectral features to spin  
 118 excitations<sup>34–36</sup> in the TSCs, as has been previously observed in spin chains of magnetic adatoms on  
 119 surfaces<sup>17</sup>. The spin excitation energies, which reflect the energy difference between the magnetic  
 120 ground state and the excited states, show a marked dependence on both  $N$  and the open-  
 121 ended/cyclic topology of the TSCs. In addition, the spin excitation amplitudes exhibit a unit-to-unit  
 122 modulation across a TSC that is linked to the spin spectral weight<sup>21</sup> (see Methods), which is the  
 123 probability of exciting the final state by means of spin-dependent electron tunneling across a given  
 124 location.

125

### 126 **Theoretical description**

127 A natural starting point to account for our experimental observations is the 1D Heisenberg  
 128 model,  $\hat{H}_{\text{Heisenberg}} = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}$  (here,  $\vec{S}_i$  denotes the spin-1 operator at site  $i$  and  $J > 0$  the  
 129 exchange coupling), where individual triangulene units are described as  $S = 1$  spins with a nearest-  
 130 neighbor antiferromagnetic exchange. However, the Heisenberg model, with  $J$  taken to be 14 meV  
 131 from STS measurements on an  $N = 2$  TSC<sup>31</sup>, fails to provide a quantitative agreement with the



132 observed spin excitation energies for oTSCs (Extended Data Fig. 3). We therefore conducted  
 133 extensive Hubbard model calculations using configuration interaction in the complete active space  
 134 (CAS) approximation, exact diagonalization (ED) and density matrix renormalization group  
 135 (DMRG), and compared them with model spin Hamiltonians solved by ED (see Methods). The  
 136 results of these calculations, and their comparison with both the energies and the modulation of the  
 137 spin excitation steps (Extended Data Fig. 4), show that the TSCs are well described by the  $S = 1$   
 138 Hamiltonian

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

139 that includes both bilinear and biquadratic exchange terms, and is referred to as the bilinear-  
 140 biquadratic (BLBQ) model (here,  $\beta$  is a parameter that determines the strength of the biquadratic  
 141 term relative to the bilinear term). From a comparison of the BLBQ and Hubbard model  
 142 calculations for an  $N = 2$  TSC, we obtain  $J = 18$  meV and  $\beta = 0.09$ , which, hereafter, we adopt for  
 143 all values of  $N$ . The emerging physical picture is that cTSCs have a unique  $S = 0$  ground state,  
 144 which is qualitatively similar<sup>8</sup> to the analytical solution obtained for  $\beta = 1/3$  – the Affleck-  
 145 Kennedy-Lieb-Tasaki (AKLT) limit<sup>7</sup> – whose ground state is the valence bond solid given by the  
 146 concatenation of singlets formed between two  $S = 1/2$  virtual spins located at adjacent triangulene  
 147 units (Fig. 2a). For oTSCs, the valence bond solid picture naturally accounts for the existence of  
 148 fractional edge states with  $S = 1/2$ , which can be Kondo screened on a metal surface, and gapped  
 149 bulk excitations. Since the terminal  $S = 1$  units in an oTSC only have a single neighbor, one of their  
 150 constituent  $S = 1/2$  spins is excluded from the valence bond solid, thus generating unpaired spins  
 151 (Fig. 2a). An effective interedge exchange couples these unpaired spins, leading to a singlet-triplet  
 152 splitting whose magnitude decays exponentially with increasing  $N$ . In contrast, complete pairing of  
 153 spins is achieved in a cTSC, and therefore no edge states are to be expected.

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

166

### 167 **Length-dependent magnetic excitations**

168 We performed a systematic experimental study of spin excitations in seventeen oTSCs with  
 169  $N$  between 2 and 20 (Fig. 3 and Supplementary Figs. 6–17), and eight cTSCs with  $N = 5, 6, 12, 13,$   
 170  $14, 15, 16$  and  $47$  (Fig. 4 and Supplementary Figs. 18–23) that validate our theoretical picture.  
 171 Figure 3 shows  $dI/dV$  spectroscopy performed on oTSCs with  $N = 2$ –6 (Fig. 3a–e) and 9 (Fig. 3f),  
 172 which reveals three principal features. First, all TSCs exhibit multiple spin excitations, with the

173 exception of the  $N = 2$  TSC, which shows a single (singlet-triplet) spin excitation at 14 meV. It is  
 174 notable that the BLBQ model accurately accounts for both the energies and amplitude modulation  
 175 of the spin excitation steps across the triangulene units for these chain lengths. The spin excitation  
 176 energies calculated by ED of the BLBQ model for TSCs with  $N \leq 16$  exhibit a good agreement  
 177 with the corresponding experimental spin excitation energies (Extended Data Fig. 6). Deviations  
 178 between theory and experiments can be partially accounted for by the renormalization of excitation  
 179 energies due to interactions with the metal surface<sup>37,38</sup>. Second, with the exception of the  $N = 3$   
 180 TSC, the energy of the lowest energy spin excitation progressively decreases with increasing  $N$ , as  
 181 predicted by the BLBQ model (Fig. 2b). Third, TSCs with  $N \geq 9$  exhibit Kondo resonances at the  
 182 terminal units, which are a hallmark of topological degeneracy and fractionalization – Kondo  
 183 resonances arise at the edges due to screening of the emergent  $S = 1/2$  edge states by the  
 184 underlying metal surface. The Kondo exchange competes with the interedge magnetic exchange,  
 185 whose magnitude decays exponentially with increasing  $N$ , but overcomes the Kondo exchange for  
 186 a small enough  $N$  (experimentally, for  $N \leq 8$ ).

187 We note that the zero-bias resonances observed at the terminal units of the  $N = 3$  oTSC  
 188 do not correspond to the emergent  $S = 1/2$  edge states, given that  $N$  is smaller than the spin  
 189 correlation length  $\zeta = 4$  (Fig. 2b). It is observed that the amplitude of the zero-bias resonance for  
 190 the  $N = 3$  oTSC is considerably lower than that of the Kondo resonances for oTSCs with  $N \geq 9$ .  
 191 We calculated the spectral function for the  $N = 3$  oTSC with a non-perturbative treatment of a  
 192 multi-orbital Anderson model (MOAM), including coupling to the surface (see Methods and  
 193 Extended Data Fig. 7). These calculations show that the zero-bias resonance in the  $N = 3$  oTSC  
 194 can be associated to a Kondo resonance of an  $S = 1$  ground state, in agreement with previous  
 195 works<sup>39</sup>. Our calculations also account for the spin excitation steps that are experimentally observed  
 196 for the  $N = 3$  oTSC. Given the large computational cost of such calculations, we presently cannot  
 197 employ them for TSCs with  $N > 3$ .

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

205

## 206 Outlook

207 The ground state of the BLBQ model in the AKLT limit, as well as its generalization in  
 208 two dimensions, are known to be a resource for universal measurement-based quantum  
 209 computation<sup>13</sup>. Our results should therefore motivate future work addressing the possibility to tune  
 210  $\beta$ , so that these non-trivial quantum states naturally occur as the ground state of coupled magnetic  
 211 nanographenes. On a general note, our on-surface synthetic protocol demonstrated here for TSCs  
 212 can be extended to afford scalable fabrication of purely organic quantum spin chains, two-  
 213 dimensional lattices and networks – thus opening exciting opportunities in the realization of non-  
 214 trivial spin liquid phases<sup>40</sup>, quantum simulators<sup>41</sup> and nanoscale spintronic devices.

215

216 **References**

- 217 1. Tsui, D. C., Stormer, H. L. & Gossard, A. C. Two-Dimensional Magnetotransport in the  
218 Extreme Quantum Limit. *Phys. Rev. Lett.* **48**, 1559–1562 (1982).
- 219 2. Laughlin, R. B. Anomalous Quantum Hall Effect: An Incompressible Quantum Fluid with  
220 Fractionally Charged Excitations. *Phys. Rev. Lett.* **50**, 1395–1398 (1983).
- 221 3. Jackiw, R. & Rebbi, C. Solitons with fermion number  $1/2$ . *Phys. Rev. D* **13**, 3398–3409 (1976).
- 222 4. Su, W. P., Schrieffer, J. R. & Heeger, A. J. Solitons in Polyacetylene. *Phys. Rev. Lett.* **42**, 1698–  
223 1701 (1979).
- 224 5. Kitaev, A. Unpaired Majorana fermions in quantum wires. *Phys.-Uspekhi* **44**, 131–136 (2001).
- 225 6. Haldane, F. D. M. Nonlinear field theory of large-spin Heisenberg antiferromagnets:  
226 semiclassically quantized solitons of the one-dimensional easy-axis Néel state. *Phys. Rev. Lett.* **50**,  
227 1153 (1983).
- 228 7. Affleck, I., Kennedy, T., Lieb, E. H. & Tasaki, H. Rigorous results on valence-bond ground  
229 states in antiferromagnets. *Phys. Rev. Lett.* **59**, 799–802 (1987).
- 230 8. Kennedy, T. Exact diagonalisations of open spin-1 chains. *J. Phys.: Condens. Matter* **2**, 5737–5745  
231 (1990).
- 232 9. White, S. R. & Huse, D. A. Numerical renormalization-group study of low-lying eigenstates of  
233 the antiferromagnetic  $S=1$  Heisenberg chain. *Phys. Rev. B* **48**, 3844–3852 (1993).
- 234 10. Gu, Z.-C. & Wen, X.-G. Tensor-entanglement-filtering renormalization approach and  
235 symmetry-protected topological order. *Phys. Rev. B* **80**, 155131 (2009).
- 236 11. Pollmann, F., Berg, E., Turner, A. M. & Oshikawa, M. Symmetry protection of topological  
237 phases in one-dimensional quantum spin systems. *Phys. Rev. B* **85**, 075125 (2012).
- 238 12. Clair, S. & de Oteyza, D. G. Controlling a Chemical Coupling Reaction on a Surface: Tools and  
239 Strategies for On-Surface Synthesis. *Chem. Rev.* **119**, 4717–4776 (2019).
- 240 13. Wei, T.-C., Affleck, I. & Raussendorf, R. Two-dimensional Affleck-Kennedy-Lieb-Tasaki state  
241 on the honeycomb lattice is a universal resource for quantum computation. *Phys. Rev. A* **86**, 032328  
242 (2012).
- 243 14. Bethe, H. Zur Theorie der Metalle. *Z. Physik* **71**, 205–226 (1931).
- 244 15. Renard, J.-P., Regnault, L.-P. & Verdagner, M. Haldane Quantum Spin Chains. in *Magnetism:  
245 Molecules to Materials I: Models and Experiments* (eds. Miller J. S. & Drillon M.) 49–93 (John Wiley &  
246 Sons, 2001).
- 247 16. Soe, W.-H., Manzano, C., De Sarkar, A., Chandrasekhar, N. & Joachim, C. Direct Observation  
248 of Molecular Orbitals of Pentacene Physisorbed on Au(111) by Scanning Tunneling Microscope.  
249 *Phys. Rev. Lett.* **102**, 176102 (2009).
- 250 17. Hirjibehedin, C. F., Lutz, C. P. & Heinrich, A. J. Spin Coupling in Engineered Atomic  
251 Structures. *Science* **312**, 1021–1024 (2006).
- 252 18. Choi, D.-J. *et al.* Colloquium: Atomic spin chains on surfaces. *Rev. Mod. Phys.* **91**, 041001 (2019).
- 253 19. Toskovic, R. *et al.* Atomic spin-chain realization of a model for quantum criticality. *Nat. Phys.* **12**,  
254 656–660 (2016).
- 255 20. Yang, K. *et al.* Probing resonating valence bond states in artificial quantum magnets. *Nat.  
256 Commun.* **12**, 993 (2021).
- 257 21. Delgado, F., Batista, C. D. & Fernández-Rossier, J. Local Probe of Fractional Edge States of  $S$   
258  $= 1$  Heisenberg Spin Chains. *Phys. Rev. Lett.* **111**, 167201 (2013).

- 259 22. Lieb, E. H. Two theorems on the Hubbard model. *Phys. Rev. Lett.* **62**, 1201–1204 (1989).
- 260 23. Fernández-Rossier, J. & Palacios, J. J. Magnetism in Graphene Nanoislands. *Phys. Rev. Lett.* **99**,
- 261 177204 (2007).
- 262 24. Clar, E. & Stewart, D. G. Aromatic Hydrocarbons. LXV. Triangulene Derivatives<sup>1</sup>. *J. Am. Chem.*
- 263 *Soc.* **75**, 2667–2672 (1953).
- 264 25. Goto, K. *et al.* A Stable Neutral Hydrocarbon Radical: Synthesis, Crystal Structure, and Physical
- 265 Properties of 2,5,8-Tri-*tert*-butyl-phenalenyl. *J. Am. Chem. Soc.* **121**, 1619–1620 (1999).
- 266 26. Inoue, J. *et al.* The First Detection of a Clar’s Hydrocarbon, 2,6,10-Tri-*tert*-Butyltriangulene: A
- 267 Ground-State Triplet of Non-Kekulé Polynuclear Benzenoid Hydrocarbon. *J. Am. Chem. Soc.* **123**,
- 268 12702–12703 (2001).
- 269 27. Pavliček, N. *et al.* Synthesis and characterization of triangulene. *Nat. Nanotechnol.* **12**, 308–311
- 270 (2017).
- 271 28. Mishra, S. *et al.* Synthesis and Characterization of  $\pi$ -Extended Triangulene. *J. Am. Chem. Soc.* **141**,
- 272 10621–10625 (2019).
- 273 29. Su, J. *et al.* Atomically precise bottom-up synthesis of  $\pi$ -extended [5]triangulene. *Sci. Adv.* **5**,
- 274 eaav7717 (2019).
- 275 30. Mishra, S. *et al.* Synthesis and characterization of [7]triangulene. *Nanoscale* **13**, 1624–1628 (2021).
- 276 31. Mishra, S. *et al.* Collective All-Carbon Magnetism in Triangulene Dimers. *Angew. Chem. Int. Ed.*
- 277 **59**, 12041–12047 (2020).
- 278 32. Lado, J. L. & Fernández-Rossier, J. Magnetic Edge Anisotropy in Graphenelike Honeycomb
- 279 Crystals. *Phys. Rev. Lett.* **113**, 027203 (2014).
- 280 33. Ternes, M., Heinrich, A. J. & Schneider, W.-D. Spectroscopic manifestations of the Kondo
- 281 effect on single adatoms. *J. Phys.: Condens. Matter* **21**, 053001 (2008).
- 282 34. Li, J. *et al.* Single spin localization and manipulation in graphene open-shell nanostructures. *Nat.*
- 283 *Commun.* **10**, 1–7 (2019).
- 284 35. Mishra, S. *et al.* Topological frustration induces unconventional magnetism in a nanographene.
- 285 *Nat. Nanotechnol.* **15**, 22–28 (2020).
- 286 36. Ortiz, R. & Fernández-Rossier, J. Probing local moments in nanographenes with electron
- 287 tunneling spectroscopy. *Progr. Surf. Sci.* **95**, 100595 (2020).
- 288 37. Oberg, J. C. *et al.* Control of single-spin magnetic anisotropy by exchange coupling. *Nat.*
- 289 *Nanotechnol.* **9**, 64–68 (2014).
- 290 38. Jacob, D., Ortiz, R. & Fernández-Rossier, J. Renormalization of spin excitations and Kondo
- 291 effect in open shell nanographenes. Preprint at <https://arxiv.org/abs/2104.02503> (2021).
- 292 39. Li, J. *et al.* Uncovering the Triplet Ground State of Triangular Graphene Nanoflakes Engineered
- 293 with Atomic Precision on a Metal Surface. *Phys. Rev. Lett.* **124**, 177201 (2020).
- 294 40. Savary, L. & Balents, L. Quantum spin liquids: a review. *Rep. Prog. Phys.* **80**, 016502 (2016).
- 295 41. Georgescu, I. M., Ashhab, S. & Nori, F. Quantum simulation. *Rev. Mod. Phys.* **86**, 153–185
- 296 (2014).
- 297
- 298 **Acknowledgements.** We thank O. Gröning and J.C. Sancho-García for fruitful discussions. This
- 299 work was supported by the Swiss National Science Foundation (grant numbers 200020-182015 and
- 300 IZLCZ2-170184), the NCCR MARVEL funded by the Swiss National Science Foundation (grant
- 301 number 51NF40-182892), the European Union’s Horizon 2020 research and innovation program

302 (grant number 881603, Graphene Flagship Core 3), the Office of Naval Research (N00014-18-1-  
 303 2708), ERC Consolidator grant (T2DCP, grant number 819698), the German Research Foundation  
 304 within the Cluster of Excellence Center for Advancing Electronics Dresden (cfaed) and  
 305 EnhanceNano (grant number 391979941), the Basque Government (Grant No. IT1249-19), the  
 306 Generalitat Valenciana (Prometeo2017/139), the Spanish Government (Grant PID2019-  
 307 109539GB-C41), and the Portuguese FCT (grant number SFRH/BD/138806/2018).  
 308 Computational support from the Swiss Supercomputing Center (CSCS) under project ID s904 is  
 309 gratefully acknowledged.

310

311 **Author contributions.** X.F., P.R. and R.F. conceived the project. F.W. and J.M. synthesized and  
 312 characterized the precursor molecules. S.M. performed the on-surface synthesis, and STM and STS  
 313 measurements. G.C., R.O. and J.F.R. performed the tight-binding, CAS, ED and DMRG  
 314 calculations. D.J. performed the MOAM-NCA calculations. K.E. and C.A.P. performed the DFT  
 315 and  $GW$  calculations. All authors contributed toward writing the manuscript.

316

317 **Competing interests.** The authors declare no competing interests.

318

319 **Fig. 1 | On-surface synthesis of triangulene spin chains and observation of zero-energy**  
 320 **edge excitations.** **a**, Chemical structure of triangulene. **b**, On-surface synthesis of TSCs using  
 321 precursor mixture **1+2**. **c**, Overview STM image after annealing the precursor mixture ( $x = 0.2$ ) on  
 322 Au(111) at 300 °C (Tunneling parameters:  $V = -0.7$  V,  $I = 70$  pA). The image is acquired with a  
 323 carbon monoxide (CO) functionalized tip. oTSCs with  $N = 2-7$  are highlighted. **d,e**, Bond-resolved  
 324 STM images of TSCs with *cis* (**d**) and *trans* (**e**) intertriangulene bonding configurations (open  
 325 feedback parameters:  $V = -5$  mV,  $I = 50$  pA;  $\Delta b = -0.7$  Å).  $\Delta b$  denotes the offset applied to the  
 326 tip-sample distance with respect to the STM setpoint above the TSCs. **f,g**, High-resolution STM  
 327 images of  $N = 16$  oTSC ( $V = -0.6$  V,  $I = 200$  pA, **f**) and cTSC ( $V = -0.7$  V,  $I = 500$  pA, **g**).  $\Delta z$   
 328 denotes the apparent height. **h,i**,  $dI/dV$  spectra acquired on every unit of the  $N = 16$  oTSC (**h**) and  
 329 cTSC (**i**), revealing zero-energy excitations exclusively at the terminal units of the oTSC (green  
 330 curves). Numerals near the curves indicate the unit number, marked in the high-resolution STM  
 331 images, on which the corresponding spectrum was acquired. The  $dI/dV$  spectra in the panels are  
 332 offset vertically for visual clarity. Open feedback parameters for the  $dI/dV$  spectra:  $V = -100$  mV,  
 333  $I = 1.4$  nA; root mean squared modulation voltage  $V_{\text{rms}} = 1$  mV.

334

335 **Fig. 2 | The valence bond solid picture and theoretical calculations of spin excitations in**  
 336 **open-ended triangulene spin chains.** **a**, Representation of triangulene as two virtual  $S = 1/2$   
 337 spins (smaller filled circles) projected over the  $S = 1$  triplet state (larger circle). Also shown is the  
 338 valence bond solid spin state for  $N = 6$  oTSC and cTSC, accounting for  $S = 1/2$  edge states in the  
 339 oTSC and their absence in the cTSC. Wavy lines denote valence bonds, which couple  $S = 1/2$  spins  
 340 from neighboring triangulene units into an  $S = 0$  singlet state. Blue and red filled circles denote spin  
 341 up and spin down electrons, respectively. **b**, Spin excitation energies calculated by ED of the BLBQ  
 342 model ( $J = 18$  meV and  $\beta = 0.09$ ) for oTSCs with  $N = 2-16$ . Size of the circles represents the spin  
 343 spectral weight. Orange circles correspond to edge excitations, while gray circles represent all other  
 344 excitations predicted by the BLBQ model up to 50 meV, which constitute more than 96% of the

345 spin spectral weight for each  $N$ . The solid line is an exponential fit to the edge excitation energies,  
 346  $\mathcal{A}e^{-N/\zeta}$ , with the prefactor  $\mathcal{A} = 19$  meV and spin correlation length  $\zeta = 4$ . **c,d**, Average  
 347 magnetization (**c**) and spin spectral weight (**d**) of the edge state of an  $N = 16$  oTSC with  $|S, S_z\rangle =$   
 348  $|1, +1\rangle$ , obtained with the BLBQ model.

349

350 **Fig. 3 | Magnetic excitations in selected open-ended triangulene spin chains and**  
 351 **comparison with the bilinear-biquadratic model. a–f**,  $dI/dV$  spectroscopy on oTSCs with  $N =$   
 352 2–6 and 9 (black curves). Representative bond-resolved STM images of oTSCs with  $N = 2–6$  are  
 353 shown (open feedback parameters:  $V = -5$  mV,  $I = 50$  pA;  $\Delta b = -0.6$  or  $-0.7$  Å). Also shown are  
 354 the unit-resolved fits to the  $dI/dV$  spectra between  $\pm 50$  mV, obtained with the BLBQ model  
 355 (orange curves;  $J = 18$  meV,  $\beta = 0.09$  and effective temperature  $T_{\text{eff}} = 5$  K). Since the BLBQ  
 356 model does not account for the underlying surface, it does not capture the Kondo exchange  
 357 phenomena. Therefore, for the terminal units of  $N = 3$  and 9 oTSCs, no fits are performed near  
 358 the Kondo resonances. Colored filled circles indicate the unique spin excitations experimentally  
 359 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,  
 360 30 and 40 mV;  $N = 6$ : 3, 27 and 40 mV;  $N = 9$ : 0, 18, 28, 30, 36 and 40 mV). Open feedback  
 361 parameters for the  $dI/dV$  spectra:  $V = -100$  mV,  $I = 600$  pA (**a**) and  $I = 1.4$  nA (**b–f**);  $V_{\text{rms}} = 1$   
 362 mV.

363

364 **Fig. 4 | Magnetic excitations in  $N = 6$  and 13 cyclic triangulene spin chains and**  
 365 **comparison with the bilinear-biquadratic model. a–d**, High-resolution STM images (**a, b**), and  
 366  $dI/dV$  spectroscopy (black curves) on every unit of  $N = 6$  (**c**) and 13 (**d**) cTSCs. The curves  
 367 marked with an asterisk in **c** and **d** denote the corresponding averaged  $dI/dV$  spectrum of all six  
 368 and thirteen units, respectively. Also shown are the fits to the averaged  $dI/dV$  spectra between  $\pm 50$   
 369 mV, obtained with the BLBQ model (orange curves;  $J = 18$  meV,  $\beta = 0.09$  and  $T_{\text{eff}} = 5$  K). **e**,  
 370 High-resolution  $dI/dV$  spectrum (black curve) for the curve indicated by an arrow in **d**, and the  
 371 corresponding  $d^2I/dV^2$  spectrum (blue curve) obtained from numerical differentiation. Colored  
 372 filled circles indicate the unique spin excitations experimentally observed for each chain length ( $N = 6$ : 15 and 42 mV;  $N = 13$ : 15, 30, 43 and 48 mV). Scanning parameters for the STM images:  $V =$   
 374  $-0.4$  V,  $I = 350$  pA (**a**) and  $V = -0.7$  V,  $I = 210$  pA (**b**). Open feedback parameters for the  $dI/dV$   
 375 spectra:  $V = -100$  mV,  $I = 1.3$  nA (**c**) and  $I = 1.4$  nA (**d**);  $V = -60$  mV,  $I = 1.4$  nA (**e**);  $V_{\text{rms}} = 1$   
 376 mV (**c, d**) and 400  $\mu$ V (**e**).

377

### 378 **Methods**

379 **Sample preparation and STM/STS measurements.** STM measurements were performed with a  
 380 low-temperature STM from Scienta Omicron operating at a temperature of 4.5 K and base pressure  
 381 below  $5 \times 10^{-11}$  mbar. Au(111) single-crystal surfaces were prepared through cycles of Ar<sup>+</sup> sputtering  
 382 and subsequent annealing at 723 K. Powder samples of precursors **1** and **2** were contained in quartz  
 383 crucibles and sublimed from a home-built evaporator at 323 K and 343 K, respectively, onto  
 384 Au(111) surface held at room temperature. STM images and  $dI/dV$  maps were recorded either in  
 385 constant-current or constant-height modes, while  $dI/dV$  spectra were recorded in constant-height  
 386 mode. For constant-height STM imaging and  $dI/dV$  mapping, feedback was opened above the  
 387 TSC. Bias voltages are provided with respect to the sample. All  $dI/dV$  measurements were obtained

388 using a lock-in amplifier (SR830, Stanford Research Systems) operating at a frequency of 860 Hz.  
389 Modulation voltages for each measurement are reported as root mean squared amplitude ( $V_{\text{rms}}$ ).  
390  $d^2I/dV^2$  spectra were obtained by numerical differentiation of the corresponding  $dI/dV$  curves,  
391 with a binomial smoothing (1–5 iterations) applied to the  $dI/dV$  curves. Unless otherwise noted,  
392 STM and STS measurements were performed with gold-coated tungsten tips. Bond-resolved STM  
393 images were acquired by scanning the TSCs with CO functionalized tips in constant-height mode.  
394 CO molecules were deposited onto a cold sample (with a maximum sample temperature of 13 K)  
395 containing the reaction products. Analysis of Kondo resonances was performed following the  
396 procedure in ref.<sup>35</sup> The data reported in this study were processed with WaveMetrics Igor Pro  
397 software.

398  
399 **DFT and GW calculations.** DFT band structure calculations of TSCs were performed with the  
400 Quantum Espresso<sup>42</sup> software package using the PBE exchange-correlation functional.<sup>43</sup> A plane  
401 wave basis with an energy cut-off of 400 Ry for the charge density was used together with PAW  
402 pseudopotentials (SSSP<sup>44</sup>). Monkhorst k-meshes of  $12 \times 1 \times 1$  and  $10 \times 1 \times 1$  were used for TSCs  
403 with two (*trans* TSC) and four (*cis* TSC) triangulene units in the periodic cell, respectively. The cell  
404 and atomic geometries were relaxed until forces were smaller than 0.001 a.u.

405 The adsorption geometry of an  $N = 6$  oTSC on Au(111) was calculated with the CP2K<sup>45</sup>  
406 software package using the PBE exchange-correlation functional together with the DFT-D3 van  
407 der Waals scheme proposed by Grimme et al.<sup>46</sup> and norm-conserving GTH pseudopotentials.<sup>47</sup> A  
408 TZV2P MOLOPT basis set<sup>48</sup> was used for C and H species, and a DZVP MOLOPT basis set for  
409 the Au species, together with a cut-off of 600 Ry for the plane wave basis set. An unrestricted  
410 Kohn-Sham approach was used for the TSCs together with an antiferromagnetic spin guess to  
411 model the magnetic ground state. The surface/adsorbate system was modeled within the repeated  
412 slab scheme, with a simulation cell containing 4 atomic layers of Au along the [111] direction and a  
413 layer of hydrogen atoms to suppress one of the two Au(111) surface states. 40 Å of vacuum was  
414 included in the simulation cell to decouple the system from its periodic replicas in the direction  
415 perpendicular to the surface. The gold surface was modeled by a supercell of  $67.80 \times 35.74$  Å<sup>2</sup>  
416 corresponding to 322 surface units. The adsorption geometry was optimized by keeping the  
417 positions of the two bottom layers of the slab fixed to the ideal bulk coordinates, while all the other  
418 atoms were relaxed until forces were lower than 0.005 eV/Å.

419 The eigenvalue self-consistent GW calculations<sup>49</sup> were performed on an  $N = 6$  oTSC with  
420 the CP2K code on the isolated geometry corresponding to the adsorption conformation. The  
421 calculations were performed based on the unrestricted DFT PBE wave functions using the GTH  
422 pseudopotentials and analytic continuation with a two-pole model. The aug-DZVP basis set from  
423 Wilhelm et al.<sup>49</sup> was used. To account for screening by the Au(111) surface, we applied the image  
424 charge model by Neaton et al.<sup>50</sup>, and to determine the image plane position with respect to the  
425 molecular geometry, we used a distance of 1.42 Å between the image plane and the first surface  
426 layer, as reported by Kharche et al.<sup>51</sup>

427 The calculations were performed using the AiidaLab platform.<sup>52</sup>

428  
429 **Derivation of the BLBQ model.** Our starting point to describe the TSCs is a tight-binding model  
430 where we only consider  $p_z$  orbitals from carbon<sup>23,53</sup>, which we refer to as the complete tight-binding  
431 model. The resulting single-particle spectrum for a TSC with  $N$  triangulenes features  $2N$  zero-

432 energy states, each hosting one electron, which arise due to the inherent sublattice imbalance in  
 433 triangulene. Strict zero-energy states occur within the nearest-neighbor tight-binding  
 434 approximation, whereas the presence of third-nearest-neighbor hopping leads to hybridization of  
 435 the zero-energy states. In order to describe the formation of local magnetic moments and their  
 436 exchange interaction, we include electron-electron interactions in the Hubbard approximation,  
 437 where only intra-atomic Coulomb repulsion ( $U > 0$ ) is considered. Comparison of the Hubbard  
 438 model with DFT calculations justifies this approximation<sup>23,53</sup>. Further, we employ the CAS  
 439 approximation, where we consider a subset of many-body states: the occupation of the set of  
 440 molecular orbitals that correspond to the  $2N$  hybridized zero-energy states is allowed to vary,  
 441 whereas the occupation of orbitals lower or higher in energy is frozen. The Hubbard model is  
 442 represented in this restricted space and diagonalized numerically. The CAS approximation for a  
 443 single triangulene and an  $N = 2$  TSC predicts  $S = 1$  and  $S = 0$  ground states, respectively<sup>31,53</sup>. The  
 444 CAS approximation allows us to obtain the spin excitation energies as a function of  $U$  for oTSCs  
 445 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-  
 446 and third-nearest-neighbor hopping parameters, respectively<sup>54</sup>). By comparing the calculated spin  
 447 excitation energies with the corresponding experimental values (Extended Data Fig. 3), we infer  $U$   
 448  $\cong 2|t_1|$ .

449 To address oTSCs with  $N > 4$ , which are beyond our current computational capabilities  
 450 using the CAS approximation, we instead use a simpler tight-binding toy model that captures the  
 451 salient features of triangulene, that is (1)  $C_3$  symmetry and (2) a sublattice imbalance of two,  
 452 resulting in two zero-energy states<sup>53</sup>. We refer to this model as the four-site model. This model has  
 453 two parameters  $t$  and  $t'$  that describe intratriangulene and intertriangulene hopping, respectively,  
 454 along a TSC (Extended Data Fig. 3). We choose  $t = -1.11$  eV and  $t' = -0.20$  eV, such that the low-  
 455 energy single-particle spectra of both the complete and the four-site tight-binding models are the  
 456 same for arbitrary chain lengths. Importantly, comparison of the low-energy many-body spectra of  
 457 an  $N = 3$  oTSC for both the complete and the four-site Hubbard models, as a function of  $U$ ,  
 458 validates this approach (Extended Data Fig. 3).

459 We can model oTSCs with  $N \leq 6$ , described with the four-site model, using DMRG as  
 460 implemented in the ITensor<sup>55</sup> library. For a fixed  $U = 1.45|t|$ , DMRG calculations are in  
 461 agreement with both the CAS approximation and experiments (Extended Data Fig. 3). Importantly,  
 462 for oTSCs with  $N = 2-6$ , the DMRG calculations match not only the experimental spin excitation  
 463 energies, but also the unit-to-unit modulation of the spin excitation amplitudes (Extended Data Fig.  
 464 4).

465 Given the large ferromagnetic exchange coupling within each triangulene unit, together  
 466 with the report of an antiferromagnetic exchange coupling between neighboring triangulene units<sup>31</sup>  
 467 and the expectation of an extremely weak magnetic anisotropy<sup>32</sup>, it would be natural to expect that  
 468 TSCs may be described by the 1D antiferromagnetic  $S = 1$  Heisenberg model. However, despite  
 469 capturing the modulation of the spin excitation amplitudes, the Heisenberg model fails to provide a  
 470 quantitative agreement of the spin excitation energies with both the experiments and Hubbard  
 471 model calculations (Extended Data Fig. 3), which implies that some correction must be lacking.  
 472 The inclusion of exchange terms beyond nearest-neighbor exchange was disregarded due to two  
 473 reasons. First, in the case of an  $N = 2$  TSC, where such corrections are obviously zero (since an  $N$   
 474  $= 2$  TSC consists of nearest-neighbor triangulene units only), we already find considerable



475 disagreement of the Heisenberg model with Hubbard model calculations (Extended Data Fig. 3).  
 476 Second, for an  $N = 3$  oTSC, we have verified that adding a second-nearest-neighbor exchange term  
 477 does not lead to an overall better agreement (Supplementary Note 2 and Supplementary Fig. 24).  
 478 As a consequence, we have considered corrections in the form of a nearest-neighbor biquadratic  
 479 exchange term, which is the simplest term compatible with all the previous arguments. The  
 480 resulting Hamiltonian is the so-called BLBQ model.

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

489 Finally, using ED of the BLBQ model, with the help of the QuSpin package<sup>56,57</sup>, we could  
 490 extend our calculations for both oTSCs and cTSCs with  $N \leq 16$ . Comparison with the  
 491 experimental data (Figs. 3 and 4) provides the final evidence that the BLBQ model describes the  
 492 TSCs.

493  
 494 **Modeling of low-bias experimental  $dI/dV$  spectra.** The calculated  $dI/dV$  spectra in the main  
 495 text are obtained using the following expression, which treats coupling to the substrate to the  
 496 lowest order<sup>58</sup>

$$\frac{dI}{dV}\Big|_n = g_0 \sum_M P_M \sum_{M', a=x,y,z} |\langle M | S_a(n) | M' \rangle|^2 \Theta_{MM'}(eV) \quad (2)$$

497 where  $n$  denotes the triangulene unit on which the  $dI/dV$  spectrum is recorded,  $M$  and  $M'$  denote  
 498 the many-body states of triangulene,  $g_0$  is a constant prefactor,  $P_M$  denotes the equilibrium  
 499 occupation of  $M$ ,  $\Theta_{MM'}(eV)$  is a thermally broadened step function centered around  $eV \pm (E_{M'} -$   
 500  $E_M)$  ( $e$  is the elementary charge), where  $E_{M'} - E_M$  is the excitation energy for a transition from  
 501 state  $M$  to  $M'$ , and  $S_a(n)$  are the  $S = 1$  spin operators acting on the  $n^{\text{th}}$  triangulene unit. The  
 502 expression for  $dI/dV$  contains the spin spectral weight, defined for the state  $M'$  and the  $n^{\text{th}}$   
 503 triangulene unit as

$$\mathcal{S}_{M'}(n) \equiv \sum_M P_M \sum_{a=x,y,z} |\langle M | S_a(n) | M' \rangle|^2 \quad (3)$$

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

509 The matrix elements in  $\mathcal{S}_{M'}(n)$  are only non-zero for states  $M$  and  $M'$  whose total spin  
 510 quantum number  $S$  differ by zero or one, reflecting the conservation of the total spin of the system  
 511 formed by the tunneling electron and triangulene. In addition, Eq. (2) contains the following sum  
 512 rule for spin-1 models: for very large  $eV$ , the unit-resolved  $dI/dV$  saturates to  $S(S+1) \times g_0 = 2g_0$ .  
 513 We have verified that by considering transition energies up to 50 meV, we have, for all TSCs

514 described by the BLBQ model, more than 92% of the spin spectral weight in each unit, and more  
 515 than 96% of the total spin spectral weight (that is, the spin spectral weight summed over all units).

516 In order to compare the experimental  $dI/dV$  spectra, which is in arbitrary units, to the  
 517 theoretical predictions given by Eq. (2), we make a fit to set the constant of proportionality  $g_0$  (we  
 518 also allow for a vertical shift that has no physical relevance). For cTSCs, where all the triangulene  
 519 units are equivalent, we average the experimental  $dI/dV$  spectra of all the units, and we perform a  
 520 single fit. In the case of oTSCs, variations of the heights of the spin excitation steps are expected  
 521 across different units<sup>21,59</sup>, so that we perform one fit for each experimental curve, using the  
 522 expression  $m(n) \times dI/dV(n) + b(n)$ , where  $m$  and  $b$  are fitting parameters. This fit assumes that the  
 523 constant of proportionality may change when the tip is moved laterally to scan across the  
 524 nanostructure, which can occur due to surface variations or minor vertical tip deviations. It must be  
 525 noted that these fitting parameters do not change the relative height of the steps in  $dI/dV$ . Thus,  
 526 only the spin spectral weight matrix elements control the relative heights in a given unit.

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

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

544 In order to solve the MOAM, NCA expands the eigenstates of the *isolated* impurity in the  
 545 coupling ( $I$ ) to the bath<sup>60</sup>. The first step is thus an exact diagonalization of the impurity  
 546 Hamiltonian. The eigenstates are simultaneously eigenstates of the total number of electrons  $N_e$   
 547 and the total spin. At half-filling ( $N_e = 6$ ), the ground state is an  $S = 1$  spin triplet, and the first and  
 548 second excited states are  $S = 0$  and  $S = 2$ , respectively. Coupling to the surface leads to fluctuations  
 549 of electrons in the impurity, and thus requires the charged sectors with  $N_e \pm 1$  electrons. The  
 550 solution yields the orbital-resolved spectral function  $\mathcal{A}_k(\omega)$  from which the atom-resolved spectral  
 551 function  $\mathcal{A}_{\text{loc}}(\omega)$  can be calculated, which is proportional to  $dI/dV$ <sup>61,62</sup>. More details on the  
 552 application of the NCA to nanoscale quantum magnets can be found in ref.<sup>63</sup>

553  
 554 **Synthesis of molecular precursors.** The synthesis of molecular precursors **1** and **2**, and associated  
 555 characterization data, are reported in Supplementary Figs. 25–49.

556

557 **References**

- 558 42. Giannozzi, P. *et al.* Quantum ESPRESSO toward the exascale. *J. Chem. Phys.* **152**, 154105 (2020).
- 559 43. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple.
- 560 *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- 561 44. Lejaeghere, K. *et al.* Reproducibility in density functional theory calculations of solids. *Science*
- 562 **351**, aad3000 (2016).
- 563 45. Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. CP2K: atomistic simulations of
- 564 condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **4**, 15–25 (2014).
- 565 46. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio
- 566 parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J.*
- 567 *Chem. Phys.* **132**, 154104 (2010).
- 568 47. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev.*
- 569 *B* **54**, 1703–1710 (1996).
- 570 48. VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular
- 571 systems in gas and condensed phases. *J. Chem. Phys.* **127**, 114105 (2007).
- 572 49. Wilhelm, J., Del Ben, M. & Hutter, J. GW in the Gaussian and Plane Waves Scheme with
- 573 Application to Linear Acenes. *J. Chem. Theory Comput.* **12**, 3623–3635 (2016).
- 574 50. Neaton, J. B., Hybertsen, M. S. & Louie, S. G. Renormalization of Molecular Electronic Levels
- 575 at Metal-Molecule Interfaces. *Phys. Rev. Lett.* **97**, 216405 (2006).
- 576 51. Kharche, N. & Meunier, V. Width and Crystal Orientation Dependent Band Gap
- 577 Renormalization in Substrate-Supported Graphene Nanoribbons. *J. Phys. Chem. Lett.* **7**, 1526–1533
- 578 (2016).
- 579 52. Yakutovich, A. V. *et al.* AiiDALab – an ecosystem for developing, executing, and sharing
- 580 scientific workflows. *Comput. Mater. Sci.* **188**, 110165 (2021).
- 581 53. Ortiz, R. *et al.* Exchange Rules for Diradical  $\pi$ -Conjugated Hydrocarbons. *Nano Lett.* **19**, 5991–
- 582 5997 (2019).
- 583 54. Tran, V.-T., Saint-Martin, J., Dollfus, P. & Volz, S. Third nearest neighbor parameterized tight
- 584 binding model for graphene nano-ribbons. *AIP Adv.* **7**, 075212 (2017).
- 585 55. Fishman, M., White, S. R. & Stoudenmire, E. M. The ITensor Software Library for Tensor
- 586 Network Calculations. Preprint at <https://arxiv.org/abs/2007.14822> (2020).
- 587 56. Weinberg, P. & Bukov, M. QuSpin: a Python package for dynamics and exact diagonalisation of
- 588 quantum many body systems part I: spin chains. *SciPost Phys.* **2**, 003 (2017).
- 589 57. Weinberg, P. & Bukov, M. QuSpin: a Python package for dynamics and exact diagonalisation of
- 590 quantum many body systems. Part II: bosons, fermions and higher spins. *SciPost Phys.* **7**, 020 (2019).
- 591 58. Fernández-Rossier, J. Theory of Single-Spin Inelastic Tunneling Spectroscopy. *Phys. Rev. Lett.*
- 592 **102**, 256802 (2009).
- 593 59. Spinelli, A., Bryant, B., Delgado, F., Fernández-Rossier, J. & Otte, A. F. Imaging of spin waves
- 594 in atomically designed nanomagnets. *Nat. Mater.* **13**, 782–785 (2014).
- 595 60. Coleman, P. New approach to the mixed-valence problem. *Phys. Rev. B* **29**, 3035–3044 (1984).
- 596 61. Jacob, D. & Kurth, S. Many-Body Spectral Functions from Steady State Density Functional
- 597 Theory. *Nano Lett.* **18**, 2086–2090 (2018).
- 598 62. Jacob, D. Simulation of inelastic spin flip excitations and Kondo effect in STM spectroscopy of
- 599 magnetic molecules on metal substrates. *J. Phys.: Condens. Matter* **30**, 354003 (2018).

600 63. Jacob, D. & Fernández-Rossier, J. Competition between quantum spin tunneling and Kondo  
601 effect. *Eur. Phys. J. B* **89**, 210 (2016).

602

603 **Data availability.** The data that support the findings of this study are available at the Materials  
604 Cloud platform (DOI: 10.24435/materialscloud:e8-aq).

605

606 **Code availability.** The custom-designed Python codes that were used for solving the bilinear-  
607 biquadratic spin Hamiltonian by exact diagonalization are available on the GitHub repository  
608 ([https://github.com/GCatarina/ED\\_BLBQ](https://github.com/GCatarina/ED_BLBQ)). All other codes are available from J.F.R.  
609 (joaquin.fernandez-rossier@inl.int) upon reasonable request.

610

611 **Additional information**

612 **Supplementary Information** is available for this paper.

613

614 **Correspondence and requests for materials** should be addressed to X.F., P.R. or J.F.R.

615

616 **Peer review information** *Nature* thanks the anonymous reviewer(s) for their contribution to the  
617 peer review of this work. Peer reviewer reports are available.

618

619 **Reprints and permissions information** is available at [www.nature.com/reprints](http://www.nature.com/reprints).

620

621 **Extended Data Fig. 1 | Scanning tunneling spectroscopy measurements of the frontier**  
622 **bands of triangulene spin chains.** **a,b**,  $dI/dV$  spectroscopy on TSCs with *cis* (**a**) and *trans* (**b**)  
623 intertriangulene bonding configurations (open feedback parameters:  $V = -1.5$  V,  $I = 250$  pA;  $V_{\text{rms}}$   
624 = 16 mV). Acquisition positions are marked with filled circles in **c** and **d**. Irrespective of the  
625 bonding configuration, TSCs exhibit an electronic band gap of 1.6 eV. **c,d**, High-resolution STM  
626 images (top panels), and constant-current  $dI/dV$  maps of the valence (middle panels) and  
627 conduction (bottom panels) bands of *cis* (**c**) and *trans* (**d**) TSCs. Scanning parameters:  $V = -0.4$  V,  $I$   
628 = 250 pA (top and middle panels, **c** and **d**) and  $V = 1.1$  V,  $I = 280$  pA (bottom panels, **c** and **d**);  
629  $V_{\text{rms}} = 30$  mV. All measurements were performed with a CO functionalized tip.

630

631 **Extended Data Fig. 2 | Density functional theory calculations on triangulene spin chains.**

632 **a,e**, DFT band structure and density of states (DOS) plots of TSCs with *cis* (**a**) and *trans* (**e**)  
633 intertriangulene bonding configurations in their antiferromagnetic ground state. Energies  $E$  are  
634 given with respect to the vacuum level. A Gaussian broadening of 100 meV has been applied to the  
635 DOS plots. Note that spin up and spin down bands are energetically degenerate. **b,f**,  
636 Corresponding band structure plots around the frontier bands.  $\vec{k}$  denotes the reciprocal lattice  
637 vector. The unit cells for the band structure calculations contain four and two triangulene units for  
638 *cis* and *trans* TSCs, respectively, with the lattice periodicities  $a = 30.0$  Å (*cis* TSC) and 17.4 Å (*trans*  
639 TSC). The dashed lines indicate the middle of the band gap. The calculations reveal nearly  
640 dispersionless frontier bands due to a weak intertriangulene electronic hybridization. In addition,  
641 TSCs exhibit a band gap of 0.68 eV irrespective of the intertriangulene bonding configurations. **c,g**,  
642 Ground state spin density distributions for *cis* (**c**) and *trans* (**g**) TSCs. Spin up and spin down  
643 densities are denoted in blue and red, respectively. **d,h**, Local DOS maps of the valence (VB) and

644 conduction (CB) bands of *cis* (**d**) and *trans* (**h**) TSCs. Spin density distributions and local DOS maps  
 645 were calculated at a height of 3 Å above the TSCs.

646

647 **Extended Data Fig. 3 | Derivation of the bilinear-biquadratic model. a,b**, Schematic energy  
 648 level diagram of  $N = 2$  (**a**) and 3 (**b**) oTSCs for the Heisenberg, Hubbard and BLBQ models.  
 649 Analytical expressions for the spin models are provided in the Supplementary Information  
 650 (Supplementary Note 2). The Hubbard model is defined such that each triangulene unit is  
 651 represented by a four-site lattice (**c**) and the many-body energy levels are computed with DMRG,  
 652 taking  $t = -1.11$  eV,  $t' = -0.20$  eV and  $U = 1.45|t|$ . The parameters of the BLBQ model ( $J = 18$   
 653 meV and  $\beta = 0.09$ ) are obtained by matching its excitation energies to those of the Hubbard model  
 654 for the  $N = 2$  TSC. **c**, Description of the four-site toy model with the intra- and intertriangulene  
 655 hopping,  $t$  and  $t'$ , respectively, indicated. The colored filled circles denote the two sublattices. **d,e**,  
 656 Comparison of the excitation energies for an  $N = 3$  oTSC computed with CAS(6,6) for the  
 657 complete Hubbard model with  $t_1 = -2.70$  eV,  $t_2 = 0$  eV and  $t_3 = -0.35$  eV (**d**), and with DMRG for  
 658 the four-site Hubbard model (**e**), as the atomic Hubbard  $U$  is varied. Dashed lines indicate the  
 659 experimental spin excitation energies of 14 meV for  $N = 2$  TSC (**a**) and, 11 and 35 meV for  $N = 3$   
 660 oTSC (**b**, **d** and **e**). Note that the Heisenberg model fails to capture both the experimental spin  
 661 excitation energies for the  $N = 3$  oTSC (**b**), and the Hubbard model results for the  $N = 2$  (**a**) and  
 662  $N = 3$  (**b**) oTSCs.

663

664 **Extended Data Fig. 4 | Experimental and theoretical spectroscopic signatures of spin**  
 665 **excitations in an  $N = 4$  open-ended triangulene spin chain.** Comparison between  
 666 experimental and theoretical (using the four-site Hubbard and BLBQ models)  $d^2I/dV^2$  spectra of  
 667 an  $N = 4$  oTSC shows a good agreement in both the energies and the modulation of the spin  
 668 spectral weight across the different units in the TSC. Numerals along the abscissa denote the unit  
 669 number of the TSC. BLBQ model calculations are performed with two different  $T_{\text{eff}}$  values for the  
 670 tunneling quasiparticle, which determine the linewidth of the  $d^2I/dV^2$  profile. Model parameters are  
 671 the same as in Extended Data Fig. 3.

672

673 **Extended Data Fig. 5 | Average magnetization for the first three  $S_z = +1$  states of an  $N =$**   
 674 **16 open-ended triangulene spin chain, obtained with the bilinear-biquadratic model.**  
 675 Calculations were performed with  $J = 18$  meV and  $\beta = 0.09$ . Orange filled circles denote the  
 676 magnetization profile of the state with the lowest excitation energy  $E = 0.4$  meV, much smaller  
 677 than the theoretical Haldane gap (9 meV), and  $|S, S_z\rangle = |1, +1\rangle$ . The average magnetization is  
 678 clearly the largest at the terminal units, and is strongly depleted at the central units, as expected for  
 679 an edge state. Blue and green filled circles denote spin excitations with energies larger than the  
 680 theoretical Haldane gap. Blue filled circles correspond to a state with  $E = 12.1$  meV and  $|S, S_z\rangle =$   
 681  $|1, +1\rangle$ , where the magnetization profile forms a nodeless standing wave with maximum average  
 682 magnetization at the central units. This can be identified as a spin wave state, except for the minor  
 683 upturn at the terminal units. Green filled circles are associated to a state with  $E = 11.6$  meV and  
 684  $|S, S_z\rangle = |2, +1\rangle$ , where the average magnetization shares similarities with both the edge and  
 685 nodeless spin wave states.

686

687 **Extended Data Fig. 6 | Theoretical and experimental spin excitation spectrum of open-**  
 688 **ended and cyclic triangulene spin chains. a,** Spin excitation energies calculated by ED of the  
 689 BLBQ model ( $J = 18$  meV and  $\beta = 0.09$ ) for oTSCs with  $N = 2-16$  (circles) and cTSCs with  $N =$   
 690  $5, 6, 12, 13, 14, 15$  and  $16$  (crosses) up to  $50$  meV. Size of the symbols accounts for the spin  
 691 spectral weight of the corresponding spin excitation. The lowest energy bulk excitation, as indicated  
 692 for the  $N = 16$  cTSC, converges to the Haldane gap ( $9$  meV) with increasing  $N$ . **b,** Experimental  
 693 spin excitation energies up to  $50$  meV for seventeen oTSCs with  $N$  between  $2$  and  $20$ , and eight  
 694 cTSCs with  $N = 5, 6, 12, 13, 14, 15, 16$  and  $47$ . The lowest energy bulk excitation, indicated for the  
 695  $N = 47$  cTSC, converges to the Haldane gap ( $14$  meV) with increasing  $N$ . Experimentally, starting  
 696 from both  $N = 16$  oTSC and cTSC, convergence to the Haldane gap is observed. Note the odd-  
 697 even effect observed for the lowest energy excitation of cTSCs, seen both in theory and  
 698 experiments.

699 **Extended Data Fig. 7 | Non-crossing approximation results for the multi-orbital Anderson**  
 700 **model of an  $N = 3$  open-ended triangulene spin chain ( $t_1 = -2.70$  eV,  $t_2 = 0$  eV,  $t_3 = -0.35$  eV**  
 701 **and  $U = 1.90|t_1|$ ) coupled to the surface ( $\Gamma/\pi = 13$  meV). a,** Total spectral function of  
 702 CAS(6,6) at different temperatures  $T$  for the case of particle-hole symmetry. **b,** Orbital-resolved  
 703 spectral function of CAS(6,6) for  $T = 4.64$  K and for the particle-hole symmetric case. **c,** Detuning  
 704 from particle-hole symmetry: total spectral function of CAS(6,6) for different values of  $\delta\varepsilon$  and  $T =$   
 705  $4.64$  K. **d,** Local spectral functions at  $T = 4.64$  K for carbon sites of one of the outer triangulene  
 706 units and the central triangulene unit ( $\delta\varepsilon = 200$  meV). The inset shows a sketch of the  $N = 3$  oTSC  
 707 with the two carbon sites marked with the corresponding colored filled circles. The spectral  
 708 functions in individual panels are offset vertically for visual clarity.  
 709









