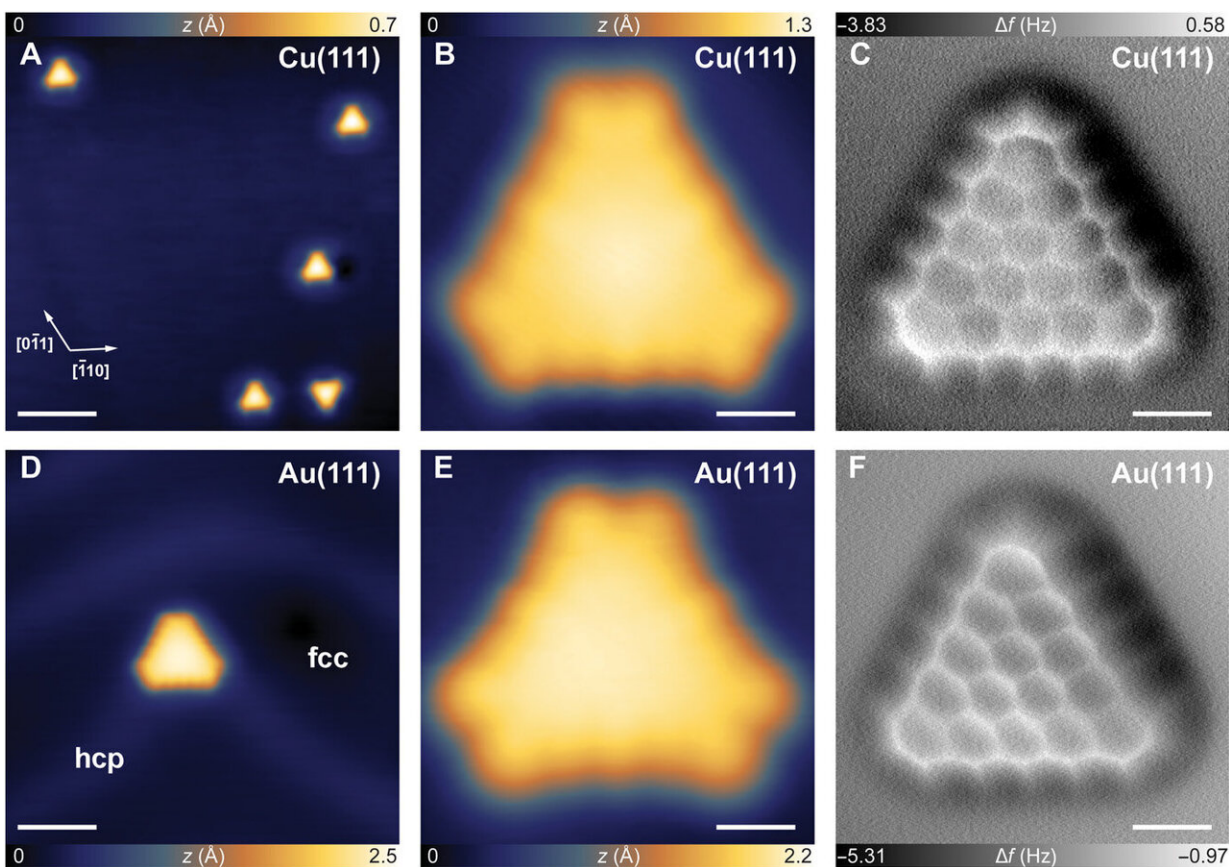


Atomically precise bottom-up synthesis of π -extended [5]triangulene

July 31 2019, by Thamarasee Jeewandara



Structural characterization of single π -extended [5]triangulene synthesized on Cu(111) and Au(111) surfaces. (A and D) Large-scale STM images of [5]triangulene molecules (A) on Cu(111) and (D) on Au(111) [(A) $V_s = -1$ V and $I = 1$ nA; scale bar, 5 nm; (D) $V_s = 1$ V and $I = 0.2$ nA; scale bar, 1.5 nm]. (B and E) Zoom-in STM images of a single [5]triangulene (B) on Cu(111) and (E) on Au(111) [(B) $V_s = -0.8$ V and $I = 1$ nA; (E) $V_s = -0.8$ V and $I = 1$ nA; scale bar, 4 Å]. (C and F) nc-AFM images of a single [5]triangulene (C) on

Cu(111) and (F) on Au(111) acquired using a CO-functionalized tip [(C) $\Delta z = 0.15 \text{ \AA}$, $V_s = 30 \text{ mV}$, $I = 0.3 \text{ nA}$; (F) $\Delta z = 0.15 \text{ \AA}$, $V_s = 10 \text{ mV}$, $I = 0.5 \text{ nA}$; scale bar, 4 \AA]. fcc, face-centered cubic; hcp, hexagonal close-packed. Credit: Science Advances, doi: 10.1126/sciadv.aav7717.

Chemists have predicted [zigzag-edged triangular graphene molecules](#) (ZTGMs) to host ferromagnetically coupled edge states, with net spin scaling with the molecular size. Such molecules can afford large spin tunability, which is crucial to engineer next-generation [molecular spintronics](#). However, the scalable synthesis of large ZTGMs and the direct observation of their edge states are a long-standing challenge due to the high chemical instability of the molecule.

In a recent report on *Science Advances*, Jie Su and colleagues at the interdisciplinary departments of chemistry, advanced 2-D materials, physics and engineering developed bottom-up synthesis of π -extended [5]triangulene with atomic precision using surface-assisted [cyclodehydrogenation](#) of a molecular precursor on metallic surfaces. Using [atomic force microscopy](#) (AFM) measurements, Su et al. resolved the ZTGM-like skeleton containing 15 fused [benzene](#) rings. Then, using [scanning tunneling spectroscopy](#) (STM) measurements they revealed the edge-localized electronic states. Coupled with supporting density functional theory calculations, Su et al. showed that [5]triangulenes synthesized on gold [Au (111)] retained an open-shell π -conjugated character with magnetic ground states.

In [synthetic organic chemistry](#), when triangular motifs are clipped along the zigzag orientation of graphene, scientists can create an entire family of zigzag-edged [triangular graphene molecules](#). Such [molecules](#) are predicted to have multiple, unpaired [\$\pi\$ -electrons](#) (Pi-electrons) and high-spin ground states with large net spin that scaled linearly with the

number of carbon atoms of the zigzag edges. Scientists therefore consider ZTGMs as promising candidates for [molecular spintronic devices](#).

The direct chemical synthesis of unsubstituted ZTGMs is a long-standing challenge due to their [high chemical instability](#). Researchers had recently adopted [a tip-assisted approach](#) to synthesize unsubstituted [3]triangulene with detailed structural and [electrical properties](#), but the method could only manipulate a single target molecule at a time. The strategy was therefore only useful for specific applications due to a lack of scalability.

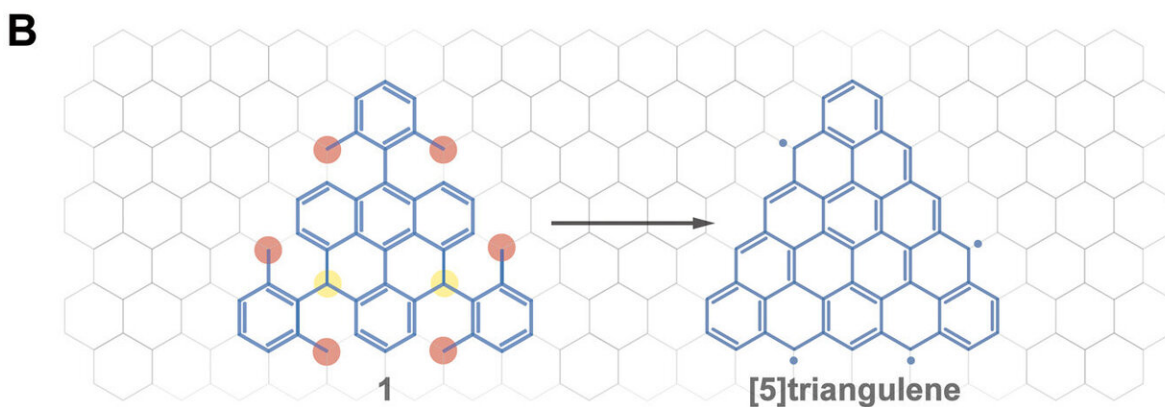
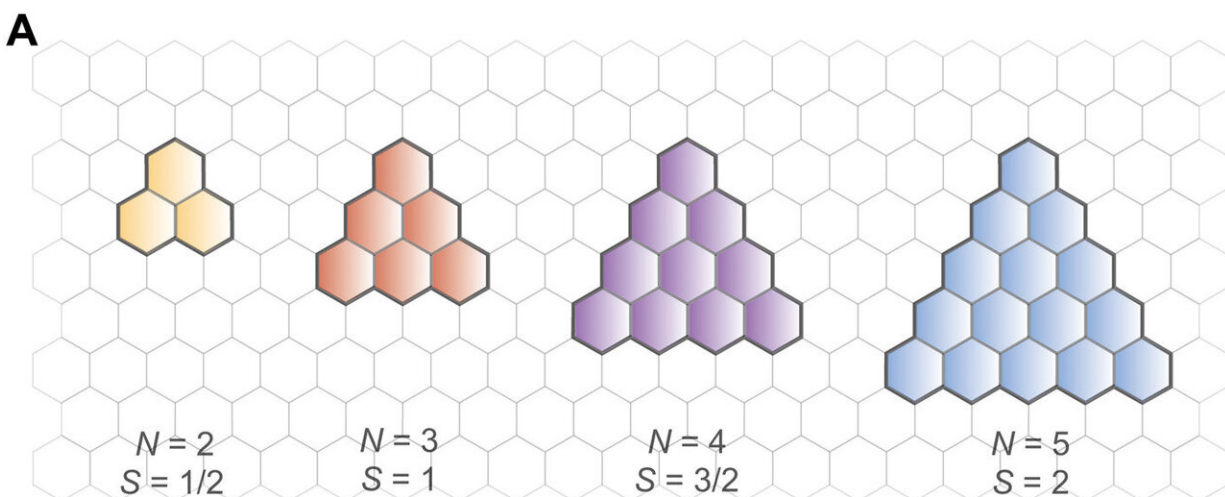


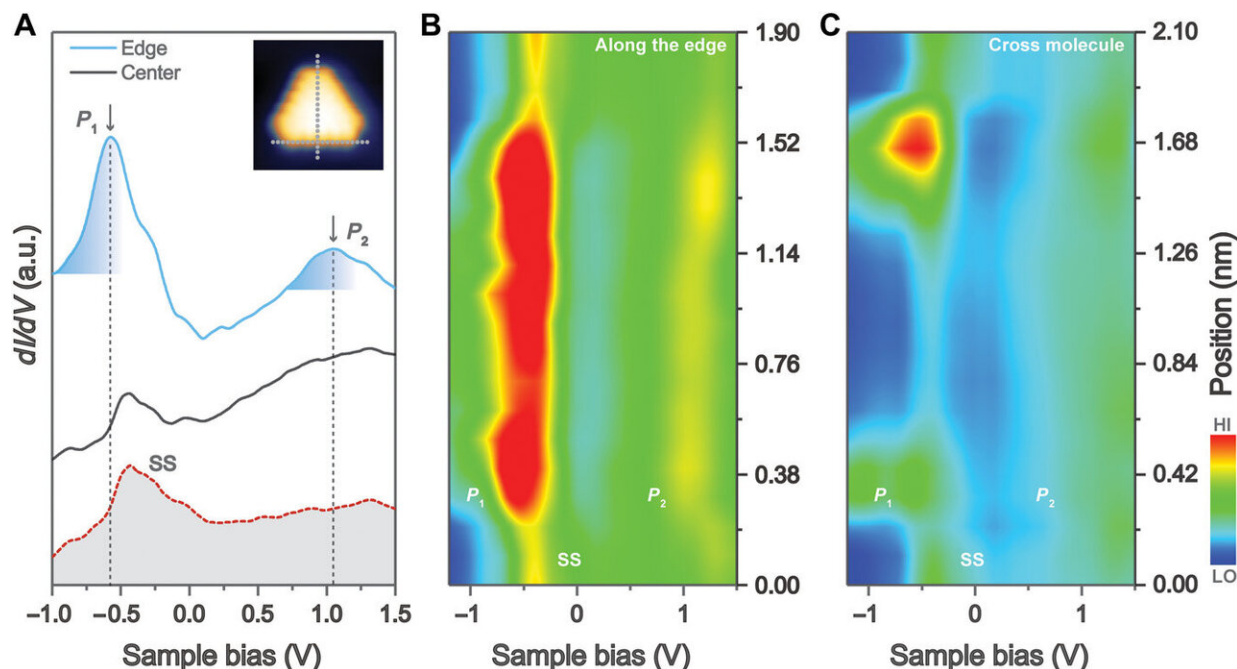
Illustration of open-shell ZTGMs and the synthetic strategy to π -extended [5]triangulene. (A) Open-shell ZTGMs with different numbers of zigzag carbon atom (N) and predicted spin multiplicity (S). Yellow, monoradical phenalenyl ($N = 2$); red, biradical triangulene ($N = 3$); violet, π -extended triradical [4]triangulene ($N = 4$); blue, tetraradical [5]triangulene ($N = 5$). (B) Schematic illustration of the surface-assisted transformation of rationally designed precursor (compound 1) to [5]triangulene. The two yellow spots indicate the sites where the on-surface dehydrogenation initiated, and the six red spots represent the methyl groups that undergo the cyclodehydrogenation process. Credit: Science Advances, doi: 10.1126/sciadv.aav7717

In comparison, a bottom-up, on-surface synthetic approach has great potential to fabricate atomically precise graphene-based nanostructures. The method typically involves cyclodehydrogenation of precursor monomers or polymerized monomers via intramolecular or intermolecular [aryl-aryl coupling](#) to predominate along the armchair direction, [instead of the zigzag direction](#). In the present work, Su et al. therefore addressed the existing challenge of designing appropriate molecular precursors to synthesize large homologs of zigzag-edged triangulenes with predicted large net spin.

The scientists first designed a unique molecular precursor to synthesize π -extended [5]triangulene. The precursor contained a central triangular core with six hexagonal rings and three 2,6-dimethylphenyl substituents attached at *meso*-positions of the core. The precursor design underwent cyclodehydrogenation and ring closure reactions on a catalytic metal surface at elevated temperatures.

To produce the well-separated target molecules of interest, the scientists deposited a low amount of precursor on the substrates and imaged them using low-temperature scanning tunneling microscopy (LT-STM) at 4.5 K. They found that annealing the precursor-decorated copper [Cu(111)]

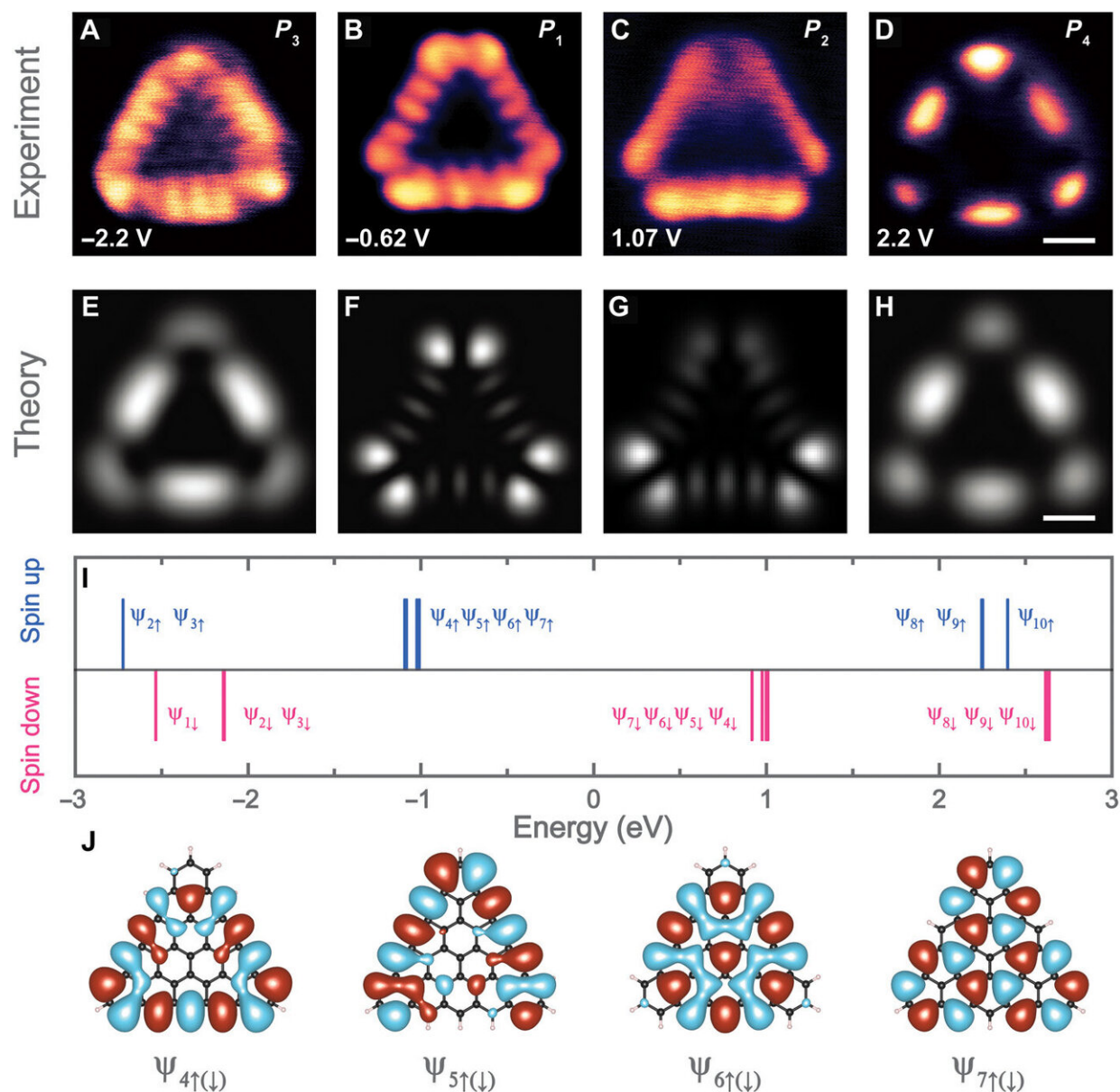
substrate induced a cyclodehydrogenation reaction at ~500 K to form flat triangle-shaped molecules. In contrast, the scientists could conduct the synthesis of [5]triangulene on the inert Au (111) substrate at a higher temperature (~600 K) to obtain a much lower yield (~5%) of the product (compared to ~60% yield on the Cu substrate).



Characterization of electronic properties of individual [5]triangulene. (A) Point dI/dV spectra acquired over different sites of the [5]triangulene molecule and the Au(111) substrate. dI/dV curves taken at the edge (solid blue line) and at the center (solid black line) of [5]triangulene and taken on the clean Au(111) surface (red dotted line). a.u., arbitrary units. (B and C) Color-coded dI/dV spectra (spaced by 0.11 nm) taken along the zigzag edge (B) and across the center of [5]triangulene [(C), starting from the apex]. The actual positions where the dI/dV spectra were taken are indicated by gray dots in the inset STM image in (A). SS, surface-state. Credit: Science Advances, doi: 10.1126/sciadv.aav7717

Su et al. used large-scale STM images to reveal well-separated triangle-shaped molecules after annealing to the precursor-decorated Cu (111) and Au (111) surfaces. They recorded the magnified STM images with a metallic tip to show that individual molecules adopted triangular/planar configurations on both substrates. At the edge of these molecules, the research team observed characteristic nodal features resembling the zigzag edges or termini of [graphene nanoribbons](#) (GNRs). When they conducted [noncontact AFM \(nc-AFM\) measurements](#) to accurately determine the chemistry of reaction products, the bright areas represented a high-frequency shift with higher electron density. As a result, they clearly resolved the zigzag-edged topology of 15 fused benzene rings, where the experimental results were in excellent agreement with those [simulated using a numerical model in a previous study](#). The observed molecular morphology therefore corresponded to the expected [5]triangulene.

The freestanding [5]triangulene contained four unpaired π -electrons as [theoretically predicted](#). To unveil the peculiar electronic properties of the molecule, Su et al. performed scanning tunneling spectroscopy (STS) measurements of single [5]triangulene grown on the weakly interacting Au (111) substrates [using a metallic tip](#). To capture the spatial distribution of the observed electron states, the scientists completed differential conductance (dI/dV) mapping on a single [5]triangulene molecule at different sample biases. On examination, the differential conductance map revealed five bright lobes located at the edge of the [5]triangulene, represented by a characteristic nodal map. The observed characteristic feature was similar to the nodal pattern of spin-polarized electronic states seen with zigzag termini and zigzag [edge of GNRs](#).

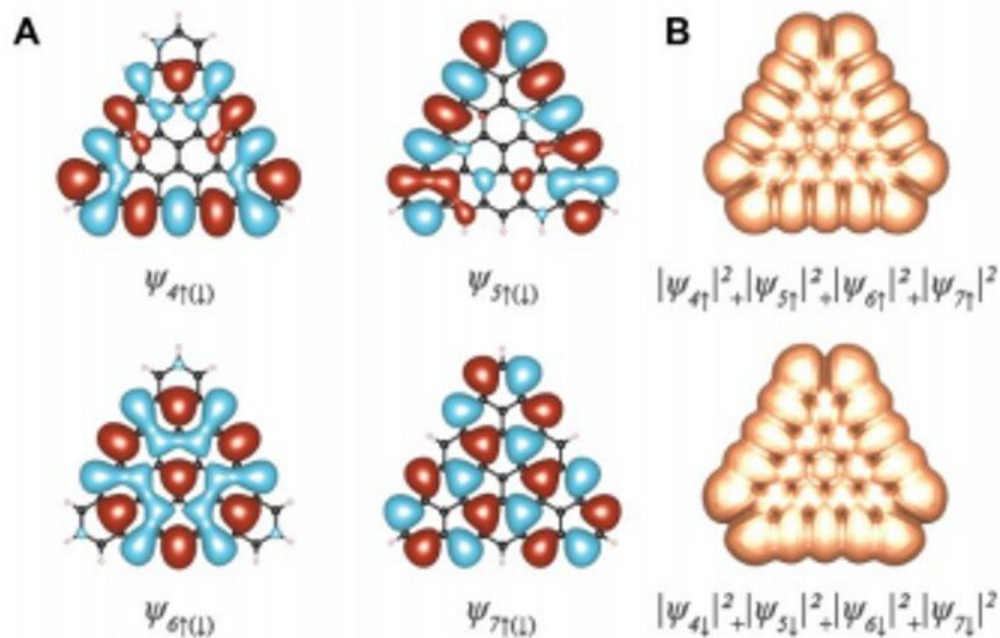


Electronic structure of [5]triangulene. (A to D) Experimental dI/dV maps recorded at different energy positions [-2.2 V for (A), -0.62 V for (B), 1.07 V for (C), and 2.2 V for (D); scale bar, 4 \AA]. (E to H) Simulated dI/dV maps of [5]triangulene acquired at different energy positions corresponding to different sets of orbitals: (E) $\psi_{2\downarrow}$ and $\psi_{3\downarrow}$, (F) $\psi_{4\uparrow}$ to $\psi_{7\uparrow}$, (G) $\psi_{4\downarrow}$ to $\psi_{7\downarrow}$ (note: the weight of $\psi_{5\downarrow}$ is set to 0.7; refer to fig. S8 for more details), and (H) $\psi_{8\uparrow}$ and $\psi_{9\uparrow}$. Scale bar, 4 \AA . (I) Calculated spin-polarized molecular orbital energies of an isolated [5]triangulene. Blue and red refers to spin-up and spin-down states, respectively. (J) DFT-calculated wave functions of four pairs of spin-polarized

orbitals [$\psi_4 \uparrow (\downarrow)$, $\psi_5 \uparrow (\downarrow)$, $\psi_6 \uparrow (\downarrow)$, and $\psi_7 \uparrow (\downarrow)$]. Red and blue colors indicate the wave functions with positive or negative values, respectively. Credit: Science Advances, doi: 10.1126/sciadv.aav7717

To gain further insights into the [5]triangulene electronic structure, Su et al. performed spin-polarized density functional theory (DFT) calculations. The energy ordering of these electron states were consistent with previous calculations of [similar graphene molecular systems](#). Additionally, the calculations also revealed a total magnetic moment of $3.58 \mu_b$ for [5]triangulene on the Au substrate, suggesting that its magnetic ground state could be retained on the Au (111) surface. The DFT (density functional theory) provided reliable information on the ground-state energy ordering and spatial shape of molecular orbitals. Su et al. observed the frontier molecular orbitals (highest-energy occupied and lowest-energy unoccupied molecular orbitals) to contain four pairs of orbitals with corresponding wave function plots.

Su et al also used the [GW method](#) of [many-body perturbation](#) to calculate the [quasiparticle](#) energies of a free [5]triangulene, where the quasiparticle gap was predicted to be 2.81 eV. They then experimentally determined the energy gap of Au-supported [5]triangulene to be ~1.7 eV consistent with [previous studies of GNRs](#) and [other molecular systems](#) of comparable size. All observations indicated a magnetic ground state of [5]triangulene on Au (111), which the scientists also validated with the DFT calculations.



The wave functions and charge densities of a free [5]triangulene. Wave function patterns and orbital densities of

In this way, Jie Su and colleagues demonstrated a feasible bottom-up approach to synthesize atomically precise unsubstituted [5]triangulene on metallic surfaces. They used nc-AFM imaging to unambiguously confirm the zigzag edge topology of the molecule and used STM measurements to resolve the edge localized electronic states. The successful synthesis of π -extended triangulenes will allow scientists to investigate magnetism and spin transport properties at the level of the single-molecule.

The scientists envision that the synthetic process will open a new avenue to engineer larger, triangular zigzag edged graphene quantum dots with atomic precision for spin and quantum transport applications. It is therefore of great interest to continue generating similar systems with diverse sizes and spin numbers to uncover their properties on a variety of

substrates using spin-polarized STM studies.

More information: Jie Su et al. Atomically precise bottom-up synthesis of π -extended [5]triangulene, *Science Advances* (2019). DOI: [10.1126/sciadv.aav7717](https://doi.org/10.1126/sciadv.aav7717)

Manuel Melle-Franco. When 1 + 1 is odd, *Nature Nanotechnology* (2017). DOI: [10.1038/nnano.2017.9](https://doi.org/10.1038/nnano.2017.9)

Yasushi Morita et al. Synthetic organic spin chemistry for structurally well-defined open-shell graphene fragments, *Nature Chemistry* (2011). DOI: [10.1038/nchem.985](https://doi.org/10.1038/nchem.985)

Pascal Ruffieux et al. On-surface synthesis of graphene nanoribbons with zigzag edge topology, *Nature* (2016). DOI: [10.1038/nature17151](https://doi.org/10.1038/nature17151)

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