Large magnetic exchange coupling in rhombus-shaped nanographenes with zigzag periphery

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Nanographenes with zigzag edges are predicted to manifest non-trivial \(\pi\)-magnetism resulting from the interplay of concurrent electronic effects, such as hybridization of localized frontier states and Coulomb repulsion between valence electrons. This provides a chemically tunable platform to explore quantum magnetism at the nanoscale and opens avenues towards organic spintronics. The magnetic stability in nanographenes is thus far greatly limited by the weak magnetic exchange coupling, which remains below the room-temperature thermal energy. Here, we report the synthesis of large rhombus-shaped nanographenes with zigzag peripheries on gold and copper surfaces. Single-molecule scanning probe measurements show an emergent magnetic spin singlet ground state with increasing nanographene size. The magnetic exchange coupling in the largest nanographene (C\(_{48}\)H\(_{18}\), containing five benzenoid rings along each edge), determined by inelastic electron tunnelling spectroscopy, exceeds 100 meV or 1,160 K, which outclasses most inorganic nanomaterials and survives on a metal electrode.

Magnetism in solids is usually associated with \(d\)- or \(f\)-block elements. However, since the isolation of graphene, the field of carbon magnetism has gained increased traction. Although ideal graphene is a diamagnetic semimetal, many of its derivative nanostructures (nanographenes) are predicted to manifest magnetism that is distinct from magnetism in molecules and solids containing transition metal atoms. First, in contrast to the localized nature of magnetic moments in transition metal atoms, unpaired electrons in nanographenes are hosted by molecular \(\pi\) orbitals, which extend over several carbon atoms. Second, the emergence of magnetic moments in nanographenes, among other theoretical interpretations\(^{2-5}\), can be understood from two competing phenomena relevant in the context of the current research: (1) hybridization energy, which is responsible for the formation of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), leading to a non-magnetic (closed-shell) ground state, and (2) electrostatic Coulomb repulsion between valence electrons, which promotes the formation of singly occupied molecular orbitals (SOMOs) hosting unpaired spins, resulting in a magnetic (open-shell) ground state. These two energy scales, along with the magnetic ordering between unpaired spins, can be efficiently tailored through a rational design of the shape, size and edge structure of nanographenes. It has long been known that hybridization energy may be strongly reduced or even completely removed in nanographenes with zigzag edges\(^{4,4}\), with higher anthenes\(^{6-11}\) and zethrenes\(^{12-14}\) being typical examples of nanographenes with open-shell characters. In recent years, this concept has also been utilized to fabricate open-shell nanographenes on surfaces, where the magnetic ground states have been directly evidenced via scanning tunnelling microscopy (STM) through the detection of Kondo interactions between localized spins and conduction electrons of the metal surfaces, and spin excitations of coupled spin systems\(^{15-19}\).

The experimental realization of nanographenes containing zigzag edges is largely restricted to structures with a mixture of zigzag and armchair edges, with prominent examples being anthenes, zethrenes and periacenes\(^{20-22}\), and synthesis of nanographenes with all sides consisting of zigzag edges (zigzag nanographenes, ZNGs) has proven challenging. Triangular ZNGs\(^{23}\), which exist as neutral radicals\(^{24,25}\), have recently been synthesized on metal and insulator surfaces under ultrahigh vacuum\(^{26-28}\). However, evidence of magnetism in these nanographenes is indirect, and relies on the detection of the probability densities attributed to the SOMOs and the associated unoccupied molecular orbitals (SUMOs) by scanning tunnelling spectroscopy (STS). Furthermore, solution synthesis of large ZNGs is limited to closed-shell systems\(^{29-32}\). In this Article, we report the on-surface synthesis of rhombus-shaped ZNGs, hereafter [\(n\)]-rhombenes, where \(n\) is the number of benzenoid rings along an edge, with \(n=4\) (C\(_{30}\)H\(_{12}\), 1) and 5 (C\(_{48}\)H\(_{18}\), 2), which represent the largest ZNGs synthesized so far (Fig. 1). Our inelastic electron tunnelling spectroscopy (IETS) measurements, supported by theoretical models, show that [\(n\)]-rhombenes acquire an open-shell ground state with increasing size. The magnetic exchange coupling (MEC) in the larger nanographene, 2, is directly determined to be 102 meV, which exceeds the room-temperature thermal energy by a factor of four, and surpasses the MEC in most known transition metal nanomagnets\(^{33}\).
Results and discussion

On-surface synthesis of [4]- and [5]-rhombenes. Our synthetic strategy for [n]-rhombenes involves the design of the molecular precursors 7,14-bis(2,6-dimethylphenyl)valene (3) and 6,13-bis[10-(2,6-dimethylphenyl)anthracen-9-yl]-1,4,8,11-tetramethylpentacene (4) (Fig. 1), which are expected to undergo surface-catalysed cyclohydrogenation and oxidative cyclization of the methyl groups, yielding 1 and 2, respectively. The synthesis of 3 (Fig. 1a) was performed starting from bisanthrone (5), which was treated with 2,6-dimethylphenylmagnesium bromide followed by dehydroxylation under an acidic condition to provide 10,12'-bis(2,6-dimethylphenyl)-9,9'-bianthracene (6). The oxidative cyclohydrogenation of 6 gave 7,14-bis(2,6-dimethylphenyl)bisanthene (7), which was subjected to twofold Diels–Alder addition with nitroethylene to obtain 3. The synthesis of 4 (Fig. 1b) was performed through the Suzuki coupling of 9-bromoanthracene (8) with (2,6-dimethylphenyl)boronic acid to afford 9-(2,6-dimethylphenyl)anthracene (9), followed by its bromination to yield 9-bromo-10-(2,6-dimethylphenyl)anthracene (10). Subsequently, 10 was lithiated to [10-(2,6-dimethylphenyl)anthracen-9-yl]lithium and reacted with 1,4,8,11-tetramethylpentacene-6,13-dione to provide 4 after reduction. Towards the synthesis of 1, 3 was deposited on a Au(111) surface, which was subsequently annealed to 300 °C to promote the on-surface reactions. High-resolution STM imaging elucidated that 92% of the molecules on the surface exhibited a uniform rhombic shape (Fig. 2a,b), and chemical structure determination via ultra-high-resolution STM imaging unambiguously proved the formation of 1 (Fig. 2c). We further attempted the on-surface synthesis of 2 from 4 using a similar strategy. An overview STM image after annealing 4 at 300 °C on Au(111) revealed the predominance of covalently coupled molecular clusters (Fig. 2d and Supplementary Fig. 1) and, in contrast to 1, we rarely found isolated molecules on the surface. Figure 2e,f presents high-resolution and ultrahigh-resolution STM images of an isolated molecule, demonstrating the successful formation of 2. The pronounced intermolecular interactions of 2 are indicative of a considerably higher reactivity of 2 compared to 1, as the propensity for 1 under identical synthetic conditions is to remain isolated on the surface. As we demonstrate below, this drastic difference in the reactivity of 1 and 2 is due to a larger zigzag periphery in 2, leading to an open-shell ground state.

To circumvent the problem of the limited yield of 2 on Au(111), we conducted the synthesis of 2 on a Cu(110) surface. In contrast to the densely packed (111) surfaces, which exhibit weak interactions with molecular adsorbates, the more open (110) surfaces feature comparatively stronger hybridization between molecular orbitals and the metal d states due to energetic upshift of the d-band centre. As a result, molecular mobility may be substantially reduced, which could prevent intermolecular reactions and increase the yield of isolated molecules. Figure 2g presents an overview STM image after deposition of 4 on Cu(110) and annealing to 240 °C. In contrast to Au(111), the reaction products on Cu(110) nearly exclusively consist of isolated molecules exhibiting a rhombic shape. The excellent match between the experimental STM image of the molecules (Fig. 2h) and the density functional theory (DFT)-simulated STM image of 2 on Cu(110) (Fig. 2i) proves the successful formation of 2.

Tunnelling spectroscopy measurements and theoretical calculations. We used STS to experimentally probe the electronic structures of 1 and 2 on Au(111). Differential conductance spectroscopy (dI/dV, where I and V denote tunnelling current and bias voltage, respectively) on 1 shows peaks in the local density of states (LDOS) at −330 mV and +400 mV (Fig. 3a). Spatially resolved
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Fig. 2 | On-surface synthesis and STM characterization of [4]- and [5]-rhombenes. a, Overview STM image after annealing 3 on Au(111) at 300 °C (V = –300 mV, I = 120 pA). b, High-resolution (V = –330 mV, I = 50 pA) and Laplace-filtered ultra-high-resolution (V = –5 mV, I = 50 pA, Δ = –0.8 Å) STM images of 1 on Au(111). Δ indicates lowering of the tip height after opening the feedback loop at the centre of the molecule. a.u., arbitrary units. c, Overview STM image after annealing 4 on Au(111) at 300 °C (V = –400 mV, I = 100 pA). Inset: high-resolution STM image of a cluster, where two constituent molecules corresponding to 2 are marked with arrows. d, High-resolution (V = –10 mV, I = 50 pA) and Laplace-filtered ultra-high-resolution (V = –5 mV, I = 50 pA, Δ = –0.9 Å) STM images of 2 on Au(111). e, Overview STM image after annealing 4 on Cu(111) at 240 °C (V = –200 mV, I = 100 pA). f, High-resolution (V = –100 mV, I = 50 pA) and DFT-simulated (V = –100 mV) STM images of 2 on Cu(111). Scale bars, 10 nm (a, d, g), 2 nm (inset, d) and 0.5 nm (all other panels). Images in b, c, e, f, h were acquired with carbon monoxide (CO)-functionalized tips.

dI/dV maps at the respective energies exhibit excellent agreement with the DFT-LDOS maps of the HOMO and LUMO of 1 on Au(111) (Fig. 3b and Supplementary Fig. 2), confirming the spectroscopic features to be molecular orbital resonances, with the HOMO–LUMO gap being 730 meV. By contrast, dI/dV spectroscopy on 2 reproducibly reveals an abrupt stepwise change in conductance that is symmetric around the Fermi energy, indicative of an inelastic excitation (Fig. 3c and Supplementary Fig. 3). The excitation threshold, extracted from a fit to the corresponding IETS spectrum, equals 102 meV (Fig. 3d).

To investigate if the inelastic excitation may be ascribed to a spin excitation, we performed DFT calculations to unravel the magnetic ground states of [n]-rhombenes. Because [n]-rhombenes have an equal number of carbon atoms in the two interpenetrating triangular sublattices of their honeycomb lattice, the ground state, as per Lieb’s theorem for bipartite lattices, is expected to be a singlet; that is, the total spin quantum number S = 0. However, this rule does not predict whether a system with S = 0 ground state is an open-shell or a closed-shell singlet. Here, this complementary information is obtained from spin-polarized DFT calculations. Figure 4a presents the DFT energy difference between the open-shell singlet and closed-shell states for a series of [n]-rhombenes in the gas phase, showing a size-dependent onset of magnetism. Although, for n ≤ 4, the ground state is closed-shell, an open-shell singlet ground state emerges for n ≥ 5, in agreement with previous reports and in support of our experimental observations. In particular, for 2, the open-shell triplet (S = 1) and closed-shell states are 100 meV and 122 meV higher in energy, respectively, compared to the open-shell singlet ground state.

We also calculated the magnetic excitation spectrum of 2 in the gas phase via an exact diagonalization of the Hubbard model at half filling—known to give results in agreement with advanced quantum chemistry methods—in the complete active space approximation with two electrons and two orbitals, with third-nearest-neighbour hopping. Figure 4b presents the energies of the manifold of excited states of 2 relative to its singlet ground state, as a function of the on-site Coulomb repulsion U. The first excited state is an open-shell triplet, with the corresponding singlet–triplet gap in the range of 75–150 meV for t₁ ≤ U ≤ 2.7t₁ (where t₁ = 2.7 eV is the nearest-neighbour hopping parameter), in close correspondence to the experimental excitation threshold of 102 meV. Figure 4c presents the gas-phase mean-field Hubbard spin polarization plot of 2, where spin-up and spin-down populations are sublattice-polarized and localized at opposite ends of the molecule. Therefore, while S = 0, a local spin polarization is maintained at each end. The corresponding picture in the case of a closed-shell ground state would entail an equal population of spin-up and spin-down electrons at every carbon atom of 2. Supplementary Fig. 4 shows the evolution of the frontier orbital gap, and the evolution of the total magnetic moment with U, for [n]-rhombenes with n = 2–7.

Finally, to establish a quantitative link between the open-shell character of 2 on Au(111) to experimental measures of electronic structure (that is, orbital resonances), we performed many-body perturbation theory GW calculations (where G and W denote Green’s function and the screened Coulomb potential, respectively), including screening effects from the underlying surface (that is, GW + IC, where IC denotes image charge). Figure 4d presents a comparative energy spectrum of the HOMO−2 to LUMO+2.
Fig. 3 | Electronic and magnetic characterization of [4]- and [5]-rhombenes. a. dI/dV spectra acquired on 1 with a CO-functionalized tip revealing HOMO and LUMO resonances at −330 mV and +400 mV, respectively (open feedback parameters: V = −600 mV, I = 200 pA (left) and V = +600 mV, I = 500 pA (right); V_ref = 16 mV). The dI/dV spectra in the panels are offset vertically for visual clarity. b. Constant-current dI/dV maps acquired with a CO-functionalized tip (upper) and corresponding DFT-LDOS maps (lower) at the HOMO and LUMO resonances of 1 on Au(111) (V = −330 mV, I = 150 pA; V_ref = 20 mV (HOMO dI/dV map) and V = +380 mV, I = 160 pA; V_ref = 24 mV (LUMO dI/dV map)). Scale bar, 0.5 nm. c,d. Background-subtracted dI/dV spectrum acquired on 2 with a CO-functionalized tip revealing inelastic excitation steps (open feedback parameters: V = −200 mV, I = 200 pA; V_ref = 4 mV) (c) and the corresponding IETS spectrum (circles, open feedback parameters: V = −200 mV, I = 2.8 nA; V_ref = 10 mV), with a fit to the experimental data using the Heisenberg dimer model (solid line) (d). The spin excitation threshold is extracted to be 102 mV. Acquisition positions for the respective dI/dV spectra are marked with a blue filled circle in the inset ultrahigh-resolution STM images in a and c. The data in c and d were acquired on different molecules with different tips.

Resonances of 2 determined from STS (Supplementary Figs. 5 and 6) and GW + IC calculations for the open-shell singlet and closed-shell states of 2. Both the Coulomb gap and the relative energies of the HOMO−2 to LUMO+2 resonances obtained from GW + IC calculations for the open-shell singlet state of 2 (Coulomb gap: 800 meV) agree well with the corresponding experimental values (fringe gap: 900 meV), while the HOMO−LUMO gap of 320 meV from the GW + IC calculation for the closed-shell state of 2 differs considerably from the experimental fringe gap, which thus provides a striking confirmation of the open-shell singlet ground state of 2 on Au(111). The GW + IC calculation was also performed for the closed-shell state of 1, where we also find a reasonable agreement of the theoretical HOMO−LUMO gap and relative energies of the HOMO−1 to LUMO+1 resonances with the corresponding experimental values (Supplementary Fig. 7), confirming the closed-shell ground state of 1 on Au(111). We also conducted dI/dV spectroscopy of 2 on Ag(111) to probe any change in the MEC (Supplementary Fig. 8), and we detected a charge transfer from Ag(111) to 2, leading to complete filling of the SOMOs and therefore a closed-shell ground state of 2. In accordance with this observation, no spin excitations are seen for 2 on Ag(111). Finally, a short note regarding the influence of the surface on the electronic structure of the ZNGs reported in our work is apt. First, charge transfer between a molecule and surface can change the occupation of molecular orbitals, which may quench magnetism46. In addition, chemisorption has been shown to lead to notable bond-order reorganization in molecules47, which may strongly influence their magnetic ground state. However, for both 1 and 2 on Au(111), charge transfer clearly does not take place because the frontier molecular orbitals of 1 (HOMO/LUMO) and 2 (SOMOs/SUMOs) are located far from the Fermi energy; moreover, 1 and 2 are physisorbed on the surface (Supplementary Fig. 9). Second, the surface will also influence the magnetic excitation spectrum55,56 of 2 both via dynamical renormalization of the excitation energy due to Kondo exchange51, and screening of $U$ and the hopping parameters52,53.

Conclusion

For robust spin-logic operations at practical temperatures, it is imperative that the MEC exceed the Landauer limit of minimum energy dissipation14 at room temperature5,6, k_B T ln(2) ≈ 18 meV, where k_B is Boltzmann’s constant and T is the temperature. The weak MEC of a few millielectronvolts commonly found in transition metal nanomagnets limits the operation of devices based on such materials to cryogenic temperatures. In recent years, this issue has been partially addressed through the synthesis of magnetic nanographenes where the MEC is either close to the Landauer limit, as in chiral graphene nanoribbon junctions15 (up to 10 meV) and triangular dimers15 (up to 14 meV), or slightly exceeds this limit, as in Clar’s goflet16 (23 meV). By comparison, the experimental singlet–triplet gap of 102 meV of 2, which provides a direct measure of the MEC, is more than five times larger than the Landauer limit—highly promising for room-temperature stable spintronics.
On a fundamental note, our results demonstrate that the synthesis of ZNGs with controlled size and shape allows building nanostructures with robust all-carbon magnetism, providing elementary building blocks to explore quantum magnetism. Given the robust MEC and negligible magnetic anisotropy in \([n]\)-rhombenes, construction of their nanoscale lattices through established on-surface synthetic techniques could pave the way for exploration of exotic low-dimensional quantum phases of matter in purely organic systems.

**Online content**

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Here, $\hat{H}_{\text{HUB}}$ is the mean-field Hubbard Hamiltonian with third-nearest-neighbor hopping:

$$\hat{H}_{\text{HUB}} = \sum_{\langle i,j \rangle, \sigma, \pi} t_{\sigma\pi} c_{i\sigma}^\dagger c_{j\pi} + U \sum_{\alpha} (n_{\alpha\uparrow} n_{\alpha\downarrow} - \frac{1}{2} n_{\alpha\uparrow} - \frac{1}{2} n_{\alpha\downarrow})$$

(1)

Here, $c_{\sigma}^\dagger$ and $c_{\sigma}$ denote the spin-selective creation and annihilation operator at sites $\sigma \in \{\uparrow, \downarrow\}$ and $\pi \in \{\pm\}$.

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**Methods**

Synthesis of molecular precursors. The detailed solution syntheses of molecular precursors 3 and 4 and the associated characterization data are reported in Supplementary Figs. 1–32.

Sample preparation and STM/STS measurements. STM measurements were performed in a commercial low-temperature STM from Scienta Omicron operating at a temperature of 4.2 K and base pressure below 5 × 10⁻¹⁰ mbar. Au(111), Ag(111) and Cu(110) single-crystal surfaces were prepared by Ar⁺ sputtering and annealing cycles. Powder samples of precursors 3 and 4 were contained in quartz crucibles and sublimed from a home-built evaporator at 270 °C and 310 °C, respectively, onto single-crystal surfaces held at room temperature. STM images and dI/dV maps were recorded in constant-current (that is, closed feedback loop) mode, and dI/dV and d2I/dV2 spectra were recorded in constant-height (that is, open feedback loop) mode. dI/dV and d2I/dV2 measurements were obtained with a lock-in amplifier operating at a frequency of 860 Hz. Modulation voltages for each measurement are reported as root-mean-squared amplitude (Vrms). Bias voltages are provided with respect to the sample. Unless otherwise noted, STM and STS measurements were performed with metallic tips. Ultrahigh-resolution STM images were acquired by scanning the molecules with CO-functionalized tips in constant-height mode, and the current channel is displayed. CO molecules were deposited on a cold sample (with a maximum sample temperature of 13 K) containing reaction products and post-deposited NaCl islands, which facilitate CO identification and pick up. The data reported in this study were processed with WaveMetrics Igor Pro or WSym software.

**Tight-binding calculations.** Tight-binding calculations were performed by numerically solving the mean-field Hubbard Hamiltonian with third-nearest-neighbor hopping:

$$\hat{H}_{\text{HUB}} = \sum_{\langle i,j \rangle, \sigma, \pi} t_{\sigma\pi} c_{i\sigma}^\dagger c_{j\pi} + U \sum_{\alpha} (n_{\alpha\uparrow} n_{\alpha\downarrow} - \frac{1}{2} n_{\alpha\uparrow} - \frac{1}{2} n_{\alpha\downarrow})$$

(1)

Here, $c_{\sigma}^\dagger$ and $c_{\sigma}$ denote the spin-selective creation and annihilation operator at sites $\sigma \in \{\uparrow, \downarrow\}$ and $\pi \in \{\pm\}$.

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Author contributions

R.F., P.R., A.N. and K.M. conceived the project. Q.C. and X.Y. synthesized and characterized the precursor molecules. S.M. performed the STM experiments. S.M. analysed the data with contributions from M.D.G. K.E. and C.A.P. performed the DFT and GW calculations. R.O., J.F.-R., J.C.S.-G., O.G. and S.M. performed the tight-binding and Hubbard calculations. All authors contributed to discussing the results and writing the manuscript.

Competing interests

The authors declare no competing interests.

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