Letter

A Single-Molecule Digital Full Adder

We-Hyo Soe,* Paula de Mendoza, Antonio M. Echavarren, and Christian Joachim

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: A specifically designed aza-starphene molecule is presented where contacting one, two, and/or three single Al adatoms allows this molecule to function as a "3-inputs & 2-outputs" digital full adder on a Au(111) surface. Sequentially positioning single Al adatoms with atomic precision to interact with aza-starphene, inputs one classical digit per Al, which is converted to quantum information by the molecule. The intramolecular logical calculations do not require a solid-state digital full adder cascade-like architecture. The measured Boolean truth table results in part from the quantum level repulsion effect and in part from a nonlinear magnetic effect also intrinsic to the aza-starphene molecule with its contacted Al adatoms.
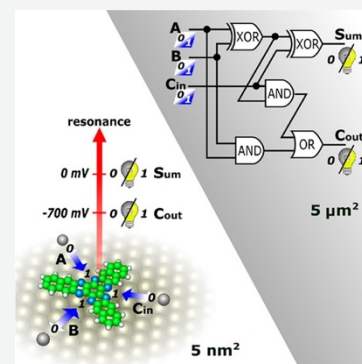
At low temperature, single-atom manipulations using a scanning tunneling microscope (LT-UHV-STM) can be used to enter analog[1] or digital[2] classical information inside a single molecule. The quantum intrinsic response of the molecule to those classical inputs is normally a shift in energy of its ground and first electronic excited states according to the required logical truth table. NOR, NAND, and XOR 2-inputs, 1-output elementary logic gates have been designed and studied experimentally this way,[2−4] following the quantum Hamiltonian computer (QHC) approach.[5] It had also been demonstrated theoretically that the QHC approach to quantum computation can reach at least the complexity of a 2 words of 2 bits digital adder without the need for cascading elementary QHC gates.[6] As presented in Figure 1 and inside a QHC molecule, the calculation scheme presented here for a 3-inputs, 2-outputs digital full adder does not demand any cascading of AND, XOR, and OR two-input logic gates as is usually the case for the design of electronic digital adders.[7]

In our experimental approach to QHC, manipulating one single metal adatom in electronic contact with the molecule is a classical action: a "0" logical binary input when there is no electronic interactions between the molecule and the adatom and a "1" logical binary input when they are. This classical one-bit information is transduced by the electronic quantum states of the molecule and is equivalent to load one bit of quantum information inside this molecule. After this transduction, the intramolecular Boolean calculations are performed. For reading the logical outputs, we measure the tunnel electronic resonance spectrum of the single molecule while inserted in a tunneling junction.[2−4] For a QHC molecule logic gate with more than one logical output, two strategies are possible for reading the logical outputs: recording those resonances (1) at
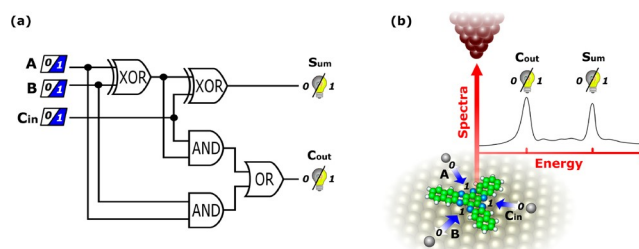

Figure 1. A "3-inputs & 2-outputs" digital full adder. (a) A standard cascade-like electronic circuit with the A, B, and C_{in} (*Carry in*) logical inputs; the elementary XOR, AND, and OR logic gates; and the Sum and C_{out} (*Carry out*) outputs involving the electrical wiring and many interconnects. (b) The studied aza-starphene QHC molecule where the chemical structure of the molecule does not show any cascading of elementary logic gates nor wiring or intramolecular interconnects. On the aza-starphene molecule, the A, B, and C_{in} logical inputs are the 3 Al adatoms and the Sum and C_{out} outputs are spectral outputs, positioning always the STM tip apex at the center of the aza-starphene molecule and recording the corresponding dI/dV tunnel spectra for reading the outputs. For this aza-starphene QHC molecule, the Sum output is positioned at a zero bias voltage and the C_{out} at −0.7 V below the metal supporting surface Fermi level. With such a recording, the saturation of the quantum repulsion effect[17] used for the QHC design is avoided for the sum (see Figure 5 for the corresponding truth table).

the same energy but at different locations along the molecule or (2) at the same location but at different energies.[6,8] For the two logical outputs digital full adder of the present study, we have followed strategy (2) as presented in Figure 1b.

We have designed the large new aza-starphene molecule (Figure 2a) by introducing 3 pyrazine molecular groups in the
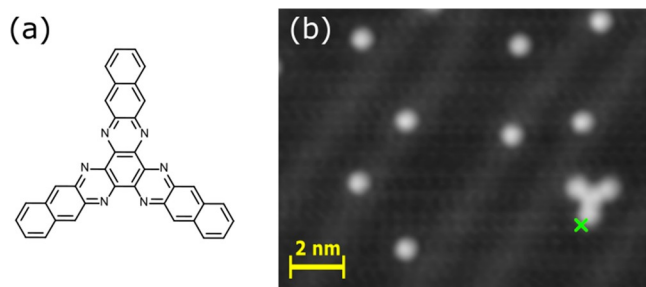

Figure 2. (a) Chemical structure of the aza-starphene molecule and (b) a large scan constant-current STM image recorded using one tip of the LT-UHV 4-STM showing the Au(111) reconstructions, one aza-starphene molecule, and 8 Al adatoms. Image conditions: 100 pA and 500 mV. Herringbone corrugation is $\Delta z = 30$ pm. The green cross indicates the STM tip apex position for recording the Figure 3 dI/dV spectrum.

central node of a long starphene.[9] For the metal inputs, we have selected single Al adatom because the oxidation state of a single Al on Au(111) is between Al(I) and Al(II).[10]

The LT-UHV-STM molecular manipulations are used to stabilize a single Al adatom in the middle of two nitrogen atoms on different branches of an aza-starphene molecule, leading to a change of its tunneling spectrum.

To benefit from the complete calculating power of our aza-starphene molecule, we have also exploited the magnetic properties of aza conjugated molecules when coordinated with Al adatoms on the Au(111) surface.[10] As described below, it brings the sum logical output of our aza-starphene molecule-adder exactly at a $V = 0$ bias voltage according to Figure 1b. It can be detected by a Kondo resonance because this molecule is demonstrating a local magnetic moment with one and three coordinated Al adatoms on the molecule physisorbed on the Au(111) surface.

The experimental results presented here were obtained with a low-temperature ultrahigh vacuum 4-STM instrument (LT-UHV 4-STM) having four independent LT-UHV-STM able on the same surface to operate in parallel with the same dI/dV spectral and atomic manipulation precisions as a single-tip LT-UHV-STM.[11] The atomically clean Au(111) single-crystal surface was prepared by repeated Ar$^+$ sputtering and heating to 780 K in UHV. The Au(111) surface was exposed to a low flux of aza-starphene molecules to obtain a very low submonolayer coverage at room temperature. This sample was then transferred to the LT-UHV 4-STM cold sample stage maintained at 4.7 K. Then, a very small amount of Al atoms was evaporated on this cold Au(111) surface through a small aperture equipped with a copper shutter through the liquid nitrogen shield of our LT-UHV 4-STM cryostat. Tungsten STM tips were electrochemically etched. STM images were recorded indistinctively on any of the four STMs of our LT-UHV 4-STM using a nominal 500 mV bias voltage and a 100 pA feedback loop set up current. After those 2 successive depositions, a typical LT-UHV STM image of the Au(111) surface is presented as in Figure 2b. The Au(111) herringbone

characteristic surface reconstruction is well imaged together with an aza-starphene molecule and the Al adatoms.

Contacting the aza-starphene with one, two, and three Al adatoms was performed by STM manipulating this molecule toward the Al and then recording successively the dI/dV electronic tunneling spectra for one, two, and three Al adatoms coordinated to the molecule. We can go backward in this logical input sequence by manipulating again the molecule away from the Al adatoms. An aza-starphene molecule was STM manipulated using a 50 MΩ tunneling junction resistance, and it reduced down to 12 MΩ with the increase of the number of Al atoms coordinated to the molecule. The dI/dV differential conductance tunneling spectra of the "STM tip−molecule−Au(111) surface" tunnel junction were recorded using a lock-in amplifier technique with an 8 mV amplitude of modulation. While ramping up and down the bias voltage on this junction, each recorded maximum defines a tunnel electronic resonance corresponding to the opening of an elastic or inelastic tunneling channel through the junction.[1,2]

The native dI/dV spectrum of a single isolated aza-starphene molecule adsorbed on Au(111) is presented in Figure 3
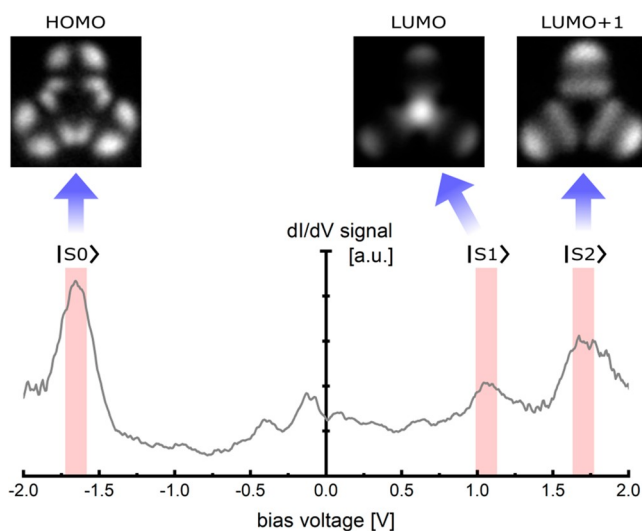

Figure 3. Native dI/dV spectrum of a free aza-starphene with its $|S0\rangle$, $|S1\rangle$, and $|S2\rangle$ tunneling resonances. Their corresponding constant-current dI/dV mapping is given and was recorded exactly at each resonance maximum. The image contrast is corresponding to the maximum monoelectronic contribution to the $|S0\rangle$, $|S1\rangle$, and $|S2\rangle$ complete electronic structure showing the HOMO, LUMO, and LUMO+1 tunneling contrast, respectively.[2] The tip position for this spectrum is indicated in Figure 1b by a green cross.

together with its so-called molecular orbital mapping. In the [−2.0 V, +2.0 V] voltage range, three electronic tunneling resonances were observed. They correspond to the $|S0\rangle$ ground and $|S1\rangle$ and $|S2\rangle$ excited state electronic resonances of the aza-starphene molecule. They are accessible via the millions of elementary hole and electron transfer processes through the molecule giving rise to the tunneling current: the $|S0+\rangle$ virtual state for $|S0\rangle$ and the $|S1-\rangle$ and $|S2-\rangle$ for the $|S1\rangle$ and $|S2\rangle$ states, respectively. At constant current, the dI/dV mapping is measuring the main monoelectronic component of those states, i.e., the one with the largest weight in the electronic state decomposition in Slater determinants and the largest effective electronic coupling between the tip end atom

apex and the surface through the molecule. When scanning the tip apex over the molecule at constant current intensity, it provides a HOMO map of $|S0\rangle$, a LUMO of $|S1\rangle$, and approximatively the LUMO+1 map of $|S2\rangle$. For this last one and when reaching the $|S2\rangle$ resonance, $|S1\rangle$ also contributes because of its tunneling resonance overlapping with the $|S2\rangle$ resonance.[12,13]

For a two logical outputs QHC molecule logic gate, as described above, there are two distinct output strategies: tracking the tunneling resonances at the same energy but at different locations along the molecule or at the same location on the molecule but at different energies.[6] As presented in Figure 4 and after a careful mapping of the aza-starphene-$(Al)_n$ complex for $n = 0$, 1, 2 and 3, there is a node of the HOMO at the center of the molecule for $n = 0$ and 1 and a maximum for $n = 2$ and 3. This is exactly what is expected for the carry logical output of a digital full adder. The sum logical output is recorded at the center of the molecular complex for $n = 1$ and 3 via the recording of a Kondo resonance. This Kondo resonance is a dI/dV spectral signature indicating that the aza-starphene-$(Al)_n$ complexes are magnetic for $n = 1$ and 3. A complete analysis of the magnetic properties of those two complexes is now further explored, in particular the value of the corresponding magnetic moment.[14] The Figure 4 dI/dV resonance location and their companion molecular orbital mapping is demonstrating how the electronic states of the aza-starphene-$(Al)_n$ complexes are shifted as a function of the number of coordinated Al adatoms. For $n = 1$, the complex is magnetic,[14] and $|S0\rangle$ and $|S1\rangle$ are moderately shift up and down in energy, respectively. For $n = 2$, the shifts up and down are more than +1 eV for $|S0\rangle$ and −0.5 eV for $|S1\rangle$. For $n = 3$, the complex is magnetic again with certainly a large magnetic moment.[14] Its $|S0\rangle$ is pushed down, but we do not succeed in observing the $|S1\rangle$ resonance in the stability voltage range of our STM experiments.

The logical operation of the aza-starphene molecule is analyzed in Figure 5 and compared with the expected full adder Boolean truth table. The Figure 5 dI/dV spectra were recorded with the STM tip end atom apex positioned on the central aza-starphene phenyl group where the logical outputs are recorded symmetrically relative to the logical inputs. In Figure 5, the raw Au(111) and noncoordinated aza-starphene dI/dV spectra are included as a reference. They illustrate the Au(111) surface state at −500 mV and the absence of tunneling electronic resonances coming from the aza-starphene in the [−1 V, +1 V] voltage range. The logic output sum resonance is recorded at 0.0 V, and the carry resonance is recorded at −0.7 V. The complete truth table of a digital full adder is verified by our aza-starphene molecule.

From the logical input to the readout, our molecule logic gate operation is very slow because of the lengthy STM single atom and molecule manipulation protocols used. Once one Al adatom coordinates to the two nitrogens on different pyrazines, the intramolecular spectral response time of the molecule will be quite fast, about a femtosecond for such a complex electronic cloud (to be compared to 10^{-16} s to stabilize the electronic cloud of a single atom[15]). This is the time interval for the aza-starphene−Al complex electronic levels to be stabilized again, for example, from the native tunneling resonance distribution of the (0, 0, 0) logical input configuration to one of the new spectra recorded for the other logical configurations. In the future, single molecular switches will certainly be incorporated in the molecular design to speed
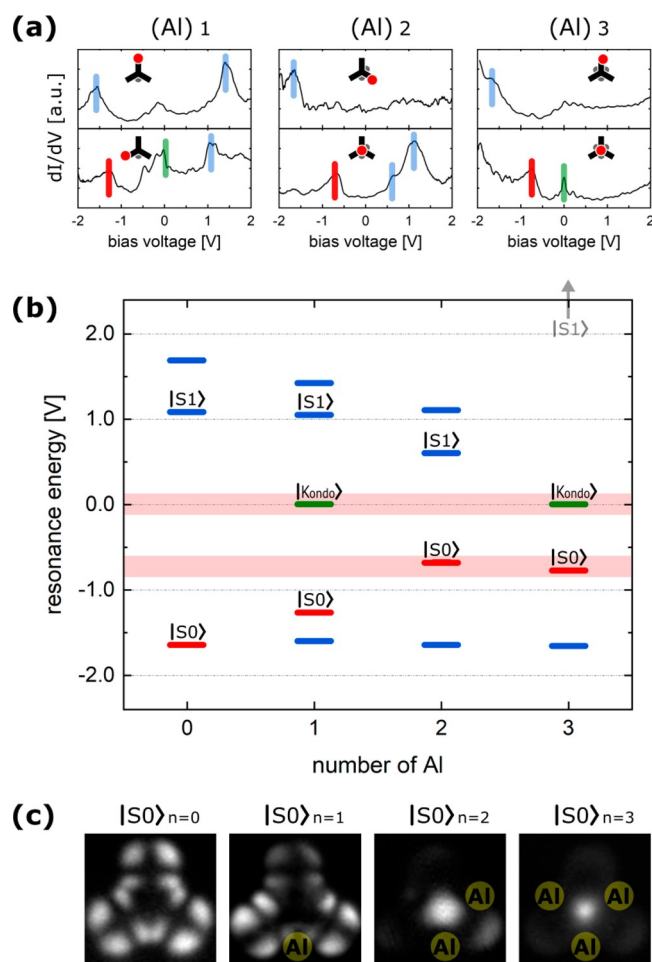

Figure 4. (a) Selected [−2 V, +2 V] voltage range dI/dV spectra to locate the tunneling resonance of the aza-starphene-$(Al)_n$ complexes as a function of the number $n = 1−3$ of Al coordinated adatom included in green (also in b) the Kondo resonance signature of a magnetic state of the complexes for $n = 1$ and $n = 3$. The difference between two spectra of each complex is the tip location (which is indicated by red dot on the simplified molecular diagram for each spectrum in panel a) during spectroscopic measurement. The shape of resonance peaks and their intensities are related to where the tip end apex state couples locally with each molecular electronic state having its own molecular orbital (MO) content distribution in real space. (c) The corresponding $|S0\rangle$ experimental molecular orbital (HOMO) mapping showing a central node for $n = 0$ and 1 and a central MO maximum for $n = 2$ and 3. For the logical output reading in panel b, the 0.0 V pink area is for the digital sum and the −0.7 V pink area is for the digital carry (see Figure 5 for the corresponding logical truth table). Notice that the $|S1\rangle$ resonance for $n = 3$ is out of the range of the dI/dV STS experiment (gray arrow up, fourth spectra column on the right in panel b).

up the logical input, for example, by using light.[16] A silicon-based 3-inputs, 2-outputs Boolean full adder actually occupies a 50 μm^2 surface area corresponding to the state-of-the-art microelectronics industry standard, whereas the same function requires only 5 nm^2 within our single molecule, i.e., 7 orders of magnitude difference. We benefit here from the fact that a QHC design does not require a cascade of elementary-to-elementary logic gates; the Boolean function results from a quantum control in the quantum state space. Finally, our strategy to calculate in the quantum state space playing with the quantum level repulsion effect can be applied on different
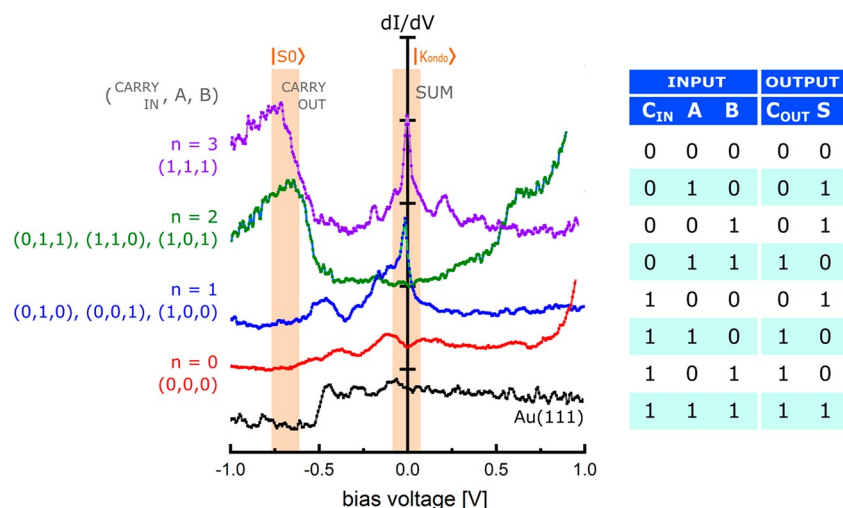
Figure 5. Detailed [−1 V, +1 V] dI/dV spectra from $n = 0$ to $n = 3$ coordinated Al-atom to the aza-starphene molecule with a specific recording of the Kondo resonance for $n = 1$ and $n = 3$. To record the dI/dV spectra, the tip apex was located on the central aza-starphene molecule where there is a maximum of conductance as presented in Figure 4. The Boolean truth table of a full binary adder is also presented. The resonance existing at −0.7 V and at 0.0 V bias voltage is encoding for a logical "1" for the Carry-out and for the Sum-out, respectively.

atomic scale supports like graphene[17] or Si(100)H[18] surfaces. The presented full adder is an experimental proof of concept that the QHC approach can go beyond the elementary "2-inputs, 1-output" logic function with an exceptional size reduction in the amount of materials required to perform a complex logic function. By using single atom/molecule manipulations, the construction of aza-starphene-(Al)$_n$ complexes with two of them being structurally asymmetric is also a nice example of the recent concept of coordination asymmetry.[19] It will certainly help in the design of more complex Boolean logic functions embedded in a single molecule.

AUTHOR INFORMATION
Corresponding Author
We-Hyo Soe − *Centre d'Elaboration de Matériaux et d'Études Structurales (CEMES), Centre National de la Recherche Scientifique (CNRS), 31055 Toulouse, France; International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Material Sciences (NIMS), Tsukuba, Ibaraki 305-0044, Japan;* orcid.org/0000-0003-2081-4039; Email: we-hyo.soe@cemes.fr

Authors
Paula de Mendoza − *Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), 43007 Tarragona, Spain*

Antonio M. Echavarren − *Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), 43007 Tarragona, Spain; Department de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, 43007 Tarragona, Spain;* orcid.org/0000-0001-6808-3007

Christian Joachim − *Centre d'Elaboration de Matériaux et d'Études Structurales (CEMES), Centre National de la Recherche Scientifique (CNRS), 31055 Toulouse, France; International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Material Sciences (NIMS), Tsukuba, Ibaraki 305-0044, Japan*

Complete contact information is available at:

https://pubs.acs.org/10.1021/acs.jpclett.1c02449

REFERENCES
(1) Manzano, C.; Soe, W.-H.; Grisolia, M.; Hliwa, M.; Joachim, C. Manipulation of a Single Molecule Ground State by means of Gold Atom Contacts. *Chem. Phys. Lett.* 2013, *587*, 35−39.

(2) Soe, W.-H.; Manzano, C.; Renaud, N.; de Mendoza, P.; De Sarkar, A.; Ample, F.; Hliwa, M.; Echavarren, A. M.; Chandrasekhar, N.; Joachim, C. Manipulating Molecular Quantum States with Classical Metal Atom Inputs: Demonstration of a Single Molecule NOR Logic Gate. *ACS Nano* 2011, *5*, 1436−1440.

(3) Skidin, D.; Faizy, O.; Krüger, J.; Eisenhut, F.; Jancarik, A.; Nguyen, K.-H.; Cuniberti, G.; Gourdon, A.; Moresco, F.; Joachim, C. Unimolecular Logic Gate with Classical Input by Single Gold Atoms. *ACS Nano* 2018, *12*, 1139−1145.

(4) Soe, W.-H.; Manzano, C.; Joachim, C. A Tetrabenzophenazine Low Voltage Single Molecule XOR Quantum Hamiltonian Logic Gate. *Chem. Phys. Lett.* 2020, *748*, 137388.

(5) Renaud, N.; Joachim, C. The Design and Stability of NOR and NAND Logic Gates Constructed with Only 3 Quantum States. *Phys. Rev. A: At., Mol., Opt. Phys.* 2008, *78*, 062316.

(6) Namarvar, O. F.; Giraud, O.; Georgeot, B.; Joachim, C. Quantum Hamiltonian Computing Protocols for Molecular Electronics Boolean Logic Gates. *Quantum Sci. Technol.* 2019, *4*, 035009.

(7) Moris Mano, M. *Digital Logic and Computer Design*; Prentice-Hall: New Jersey, 1979.

(8) Jensen, P. W. K.; Jin, C.; Dallaire-Demers, P.; Aspuru-Guzik, A.; Solomon, G. C. Molecular Realization of a Quantum NAND Tree. *Quantum Sci. Technol.* 2019, *4*, 015013.

(9) Soe, W.-H.; Manzano, C.; de Mendoza, P.; McGonigal, P. R.; Echavarren, A. M.; Joachim, C. Long Starphene Single Molecule NOR Boolean Logic Gate. *Surf. Sci.* 2018, *678*, 163−168.

(10) Soe, W.-H.; Manzano, C.; Robles, R.; Lorente, N.; Joachim, C. On-Surface Atom-by-Atom-Assembled Aluminum Binuclear Tetra-

benzophenazine Organometallic Magnetic Complex. *Nano Lett.* 2020, *20*, 384−388.

(11) Yang, J.; Sordes, D.; Kolmer, M.; Martrou, D.; Joachim, C. Imaging, Single Atom Contact and Single Atom Manipulation at Low Temperature using the New ScientaOmicron LT-UHV 4 STM. *Eur. Phys. J.: Appl. Phys.* 2016, *73*, 10702.

(12) Krüger, J.; Eisenhut, F.; Skidin, D.; Lehmann, T.; Ryndyk, D. A.; Cuniberti, G.; Garcia, F.; Alonso, J. M.; Guitián, E.; Pérez, D.; et al. Electronic Resonances and Gap Stabilization on Higher Acenes on a Gold Surface. *ACS Nano* 2018, *12*, 8506−8511.

(13) Eisenhut, F.; Kühne, T.; Garcia, F.; Fernández, S.; Guitián, E.; Pérez, D.; Trinquier, G.; Cuniberti, G.; Joachim, C.; Peña, D.; et al. Dodecacene Generated on Surface: Reopening of the Energy Gap. *ACS Nano* 2020, *14*, 1011−1017.

(14) Soe, W.-H.; Robles, R.; de Mendoza, P.; Echavarren, A. M.; Lorente, N.; Joachim, C. Doublet-Singlet-Doublet Transition in a Single Organic Molecule Magnet On-Surface Constructed with up to 3 Aluminum Atoms, *Nano Lett.* 2021 (submitted).

(15) Kienberger, R.; Goulielmakis, E.; Uiberacker, M.; Baltuska, A.; Yakovlev, V.; Bammer, F.; Scrinzi, A.; Westerwalbesloh, Th.; Kleineberg, U.; Heinzmann, U.; et al. Atomic Transient Recorder. *Nature* 2004, *427*, 817−821.

(16) Wen, Y.; Yi, W.; Meng, L.; Feng, M.; Jiang, G.; Yuan, W.; Zhang, Y.; Gao, H.; Jiang, L.; Song, Y. Photochemical-Controlled Switching Based on Azobenzene Monolayer Modified Silicon (111) Surface. *J. Phys. Chem. B* 2005, *109* (30), 14465−14468.

(17) Srivastava, S.; Kino, H.; Joachim, C. Quantum Half-Adder Boolean Logic Gate with a Nano-Graphene Molecule and Graphene Nano-Electrodes. *Chem. Phys. Lett.* 2017, *667*, 301−306.

(18) Kolmer, M.; Zuzak, R.; Dridi, G.; Godlewski, S.; Joachim, C.; Szymonski, M. Realization of a Quantum Hamiltonian Boolean Logic Gate on the Si(001):H Surface. *Nanoscale* 2015, *7*, 12325−12330.

(19) Ariga, K.; Shionoya, M. Nanoarchitectonics for Coordination Asymmetry and Related Chemisty. *Bull. Chem. Soc. Jpn.* 2021, *94*, 839−859.