

Manipulating Molecular Quantum States with Classical Metal Atom Inputs: Demonstration of a Single Molecule NOR Logic Gate

We-Hyo Soe,^{†,*} Carlos Manzano,[†] Nicolas Renaud,[‡] Paula de Mendoza,[§] Abir De Sarkar,[†] Francisco Ample,[†] Mohamed Hliwa,[‡] Antonio M. Echavarren,[§] Natarajan Chandrasekhar,[†] and Christian Joachim^{†,*}

[†]IMRE, A*STAR (Agency for Science, Technology and Research), 3 Research Link, 117602, Singapore, [‡]CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France, and [§]Institute of Chemical Research of Catalonia (ICIQ), Avenida Països Catalans 16, 43007 Tarragona, Spain

Digital logic gates are basic functional units ubiquitously found in any digital electronic circuit performing arithmetic logic operations. The most straightforward approach for improving the performance of electronic circuits is the further miniaturization of solid state transistors to increase the density per wafer area. For overcoming the foreseeable technical and fundamental problems limiting the transistor miniaturization down to the atomic scale, new paradigms have been proposed like molecular electronics and quantum computing.^{1,2} In this regard, single molecular logic gates have been constructed by manipulating CO molecules to assemble molecular cascades using mechanical information transfer from molecule to molecule in the cascade to perform logic operations.³ Another approach is to use intramolecular proton transfer tautomerism for inducing a topological rotation in the frontier molecular orbitals of a naphthalocyanine molecule and to influence the electronic states of neighboring molecules.⁴ In a classical-like architecture, a supramolecular assembly of those molecules was also proposed for constructing logic gates.⁵ Here, we demonstrate that the intramolecular quantum state control together with classical inputs permits embedding the complexity of a logic gate into a single molecule. Scanning tunnelling microscope (STM) differential conductance measurements show that the NOR logic gate function manifests as measurable energy shifts of molecular orbitals, upon the contact of a molecule with Au atoms acting as the classical inputs. Our results indicate a method for future development of complex Boolean logic gates using a single molecule

ABSTRACT Quantum states of a trinaphthylene molecule were manipulated by putting its naphthyl branches in contact with single Au atoms. One Au atom carries 1-bit of classical information input that is converted into quantum information throughout the molecule. The Au–trinaphthylene electronic interactions give rise to measurable energy shifts of the molecular electronic states demonstrating a NOR logic gate functionality. The NOR truth table of the single molecule logic gate was characterized by means of scanning tunnelling spectroscopy.

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associated with an appropriate Quantum Hamiltonian Computing (QHC) design (see Supporting Information) running under the superposition principle using a tunnel junction as a source of nonstationary quantum electronic states.

Model and Experimental Systems. When a quantum system described by a valence bond-like $H(\alpha, \beta)$ Hamiltonian (represented in Figure 1a by the spatial distribution of its seven valence bondlike states) is prepared in the initial nonstationary state $|\phi_{\text{tip}}\rangle$, the resulting effective Rabi-like oscillation frequency $\Omega(\alpha, \beta)$ from this $|\phi_{\text{tip}}\rangle$ driving state to the output target state $|\phi_{\text{sub}}\rangle$ can follow a Boolean truth table according to the α and β classical binary inputs, “0” or “1”. The $H(\alpha, \beta)$ eigenvalues and eigenvectors depend on (α, β) , converting the classical binary information carried by the α and β digits in quantum information available all over the quantum system according to the corresponding change of its eigenstates. When $|\phi_{\text{tip}}\rangle$ and $|\phi_{\text{sub}}\rangle$ are interconnected to metallic pads, the tunnelling current intensity passing through this seven quantum states system (Figure 1a) is proportional to $\Omega^2(\alpha, \beta)$.⁶ The quantum system consisting of a central

*Address correspondence to wh-soe@imre.a-star.edu.sg.

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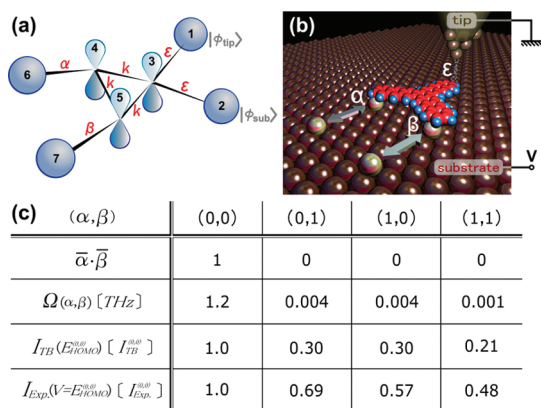


Figure 1. Schematic view of a QHC quantum system leading to a NOR gate, the corresponding experimental setup, and the resulting NOR truth table. (a) The seven valence bond-like quantum states model of a QHC logic gate whose $H(\alpha, \beta)$ Hamiltonian can be tuned to behave as a NOR gate (see Supporting Information). (b) The experimental implementation of a trinaphthylene molecule NOR gate where the “tip ↔ output branch end ↔ Au(111) surface” tunnel junction is used to measure the logic status of the NOR gate via the tunnel current intensity. (c) NOR truth table: the calculated Rabi-like oscillation frequency $\Omega(\alpha, \beta)$ is given in the second line for a weak measurement coupling $\varepsilon = 0.001$ eV, the normalized calculated current intensity is in the third line, and the measured one, using the Figure 1b configuration, is in the fourth line. The current intensities were calculated by interconnecting the $|\phi_{tip}\rangle$ and $|\phi_{sub}\rangle$ states to a semi-infinite chain and calculating the corresponding transmission coefficient through the seven quantum states, shown in Fig 1a, which is considered as the scattering defect.⁹ The current intensity outputs are normalized using the current amplitude at the HOMO energy position as a reference for the (0,0) input configuration. For calculated $\Omega(\alpha, \beta)$ and I_{TB} , the (α, β) scalar values are 0.0 and 1.0 eV. For the experimental I_{Exp} , the encoding is simply “0” Au atom out and “1” Au atom in. Using PM6-Cl calculations (see Supporting Information), the α and β values can be calculated and the detail molecular electronic structure of the trinaphthylene molecule mapped to a valence bondlike model.¹⁸

triangle and two inputs shown in Figure 1a, with three and two quantum states, respectively, can be a NOR, a NAND, or a XOR gate depending on its corresponding $H(\alpha, \beta)$ detailed matrix structure (see Supporting Information and the NOR answer in the Figure 1c table).

The trinaphthylene molecule was selected because of its starlike topology whose π frontier molecular orbital symmetry is similar to one of the three quantum states central triangle system presented in Figure 1a. The three naphthyl branches are conjugated with the central phenyl in charge of the quantum communication between the two input branches and the output branch (Figure 1b). The trinaphthylene molecule is physisorbed on Au(111) to preserve the spatial extension of the molecular orbitals and to open space between the molecular board and the surface so that manipulated single Au atoms contact from beneath the molecular board. Classical binary information, “1” or “0”, is input by contacting or detaching one Au atom per naphthyl branch. One Au atom contacting the naphthyl branch accounts for a logical “1”. To measure the logic gate output, the STM tip apex is positioned at the end of the

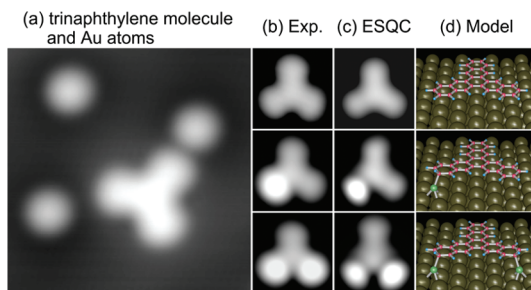


Figure 2. Experimental and theoretical topographic images of a trinaphthylene molecule with 0, 1, and 2 Au-atom inputs. (a) Constant-current STM image, $4 \text{ nm} \times 4 \text{ nm}$, of a trinaphthylene molecule and 3 Au adatoms on Au(111) recorded at $I = 640 \text{ pA}$ and $V = 100 \text{ mV}$. (b) Experimental topographic images ($2 \text{ nm} \times 2 \text{ nm}$) corresponding, from the top, to the three (0,0), (1,0) and (1,1) input configurations, and (c) the corresponding calculated STM-ESQC images at a constant tunnelling current of 1 pA. (d) ASED+ optimized structures obtained after comparing the experimental and calculated STM images. Experimental images show that Au atoms are attached slightly out of mirror symmetry planes perpendicular to the molecular board.

third branch of the trinaphthylene molecule to perform tunnelling spectroscopy so that variations in the electronic spectra of the molecule due to Au atom inputs are monitored (Figure 1b). Each classical input interacting with one naphthyl end locally perturbs the delocalized quantum structure of the frontier molecular π orbitals (see Supporting Information).⁷ The corresponding molecule π system reorganization is visible in differential conductance (dI/dV) maps for each input combination as well as in the tunnelling spectra. Because of trinaphthylene's QHC molecular design, this reorganization was expected to produce a NOR truth table, revealing the NOR functionality of a single trinaphthylene molecule when interconnected as presented in Figure 1b. Another π molecular orbital structure will find its molecular states shifted differently in answer to the Au atom input contacts.

RESULTS AND DISCUSSION

The three (α, β) input configurations (0,0), (1,0) and (1,1) of our NOR gate are presented in Figure 2 with none, one, and two Au atoms manipulated at the input ends of a trinaphthylene molecule. In each case, the final molecule conformation and the position of the Au atoms at its naphthyl ends were determined by comparing experimental and calculated STM-elastic scattering quantum chemistry (ESQC)^{8,9} images. The atomic superposition and electron delocalization (ASED+)^{10,11} molecular mechanics routine was used to extract the optimum molecule–surface conformation so that the experimental and calculated images converge (see Supporting Information). These calculations reveal that putting one Au atom in contact with the end of a naphthyl branch deforms its terminal phenyl group while subtly lifting up the corresponding H .⁷

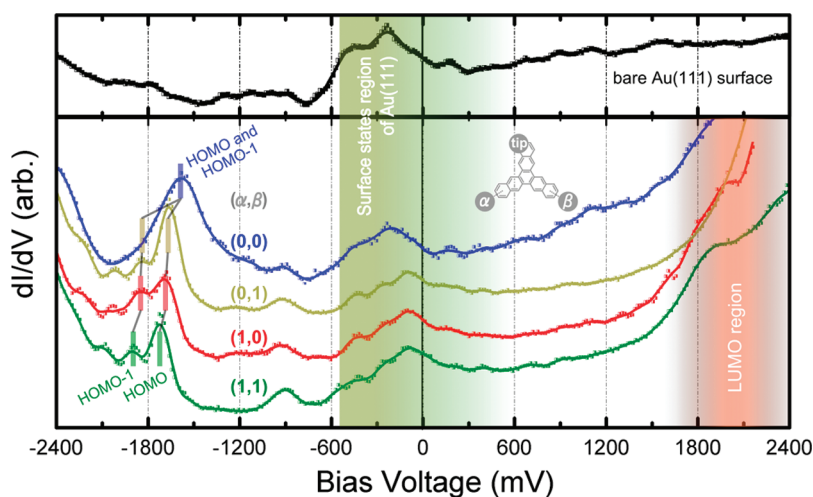


Figure 3. dI/dV spectra for four Au–trinaphthylene molecule configurations. While a broad peak corresponding to the LUMO appears in all configurations at the positive bias, a distinct peak in the negative regime observed on a bare molecule is split and shifted by Au atom inputs. The HOMO of the molecule in gas phase, with a 3-fold symmetry, and the degenerated HOMO-1 and HOMO-2 orbitals, with 2-fold and mirror symmetries, are very close to the same energy level. However once adsorbed on a substrate this degeneracy unravels due to symmetry constraints resulting in the HOMO-2 orbital being dropped out from this energy range. Therefore the peak at -1600 mV in the spectrum taken from a bare molecule consists of only HOMO and HOMO-1. The surface state of Au(111) is provided as a reference.

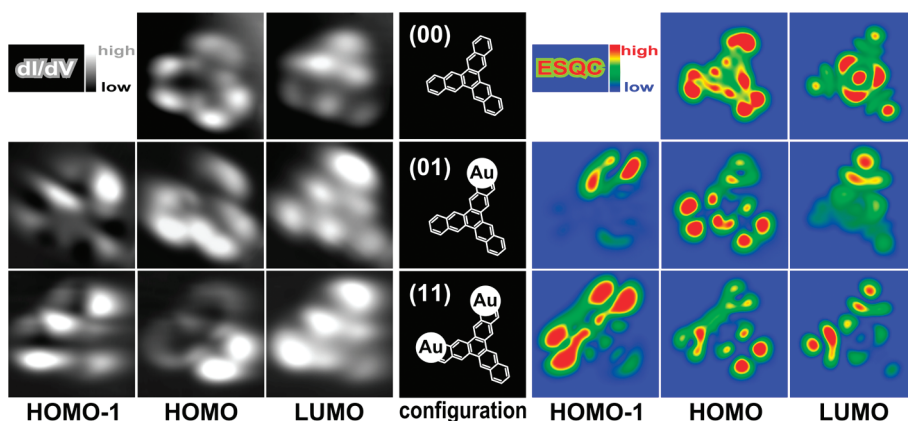


Figure 4. Experimental and theoretical differential conductance maps at LUMO, HOMO, and HOMO-1 energy positions for each input configuration. Three columns on the left show constant-current dI/dV maps recorded at voltages indicated by the bars in Figure 3. The tunnelling currents set for mapping are between 1.5 and 5.0 nA. The corresponding calculated STM-ESQC images, at a constant tip height of 0.73 nm from surface, are displayed on the right side. Experimental HOMO and LUMO images of the (0,0) input configuration appear slightly distorted because the molecule is bound to a herringbone kink of the reconstructed Au(111) surface. All experimental images are $2.5 \text{ nm} \times 2.5 \text{ nm}$, and the ESQC images are $2.0 \text{ nm} \times 2.0 \text{ nm}$.

After having the classical (0,0), (1,0), and (1,1) input configurations readily available, the STM tip was positioned on the output branch of the molecule to read/measure its NOR logical status as a function of the inputs as indicated in Figure 1b. To extract a maximum amount of information on what is happening quantum mechanically from the input branches, a reference constant current STM dI/dV map of the trinaphthylene molecule in the (0,0) configuration was recorded. These maps allow visualizing the maximum lateral spatial extension of its frontier molecular orbitals. A dI/dV spectrum of the molecule was recorded to determine the energy position of its ground, *via* its first oxidized (HOMO) state, and first reduced (LUMO) states. Since the LUMO is usually much broader than the HOMO,¹²

the HOMO was selected as a reference energy position in the dI/dV spectrum to measure the logical output status of the gate. The large LUMO broadening is due to its close proximity to the vacuum level as compared to the HOMO state. It obscures any molecular orbital splitting or shift that can occur as a function of the Au input configuration.

Observation of the NOR gate functioning results from systematically recording dI/dV spectra for each of the four input configurations (0,0), (0,1), (1,0), and (1,1) with the tip apex positioned on a HOMO spatial maximum at the end of the output naphthyl branch. As expected from the molecule design, the first oxidation state of the molecule is shifted down as a function of the number of Au inputs. In the HOMO–LUMO gap voltage

range, small resonances resulting from the superposition of surface states with the Au states appear as shown in Figure 3. Measured at the fixed bias voltage corresponding to the (0,0) HOMO resonance, variations in the tunnelling current intensity can be tabulated in a Boolean-like truth table (see the fourth row in Figure 1c) demonstrating that a single trinaphthylene molecule performs the logic function of a NOR gate.

To better understand the functioning of our single molecule NOR gate, we have performed full semi-empirical PM6-Cl molecular electronic states calculations¹³ to follow how the ground and first excited states of the Au-molecule evolve as a function of the number of Au atoms input (see Supporting Information). Those calculations confirm that the ground state is shifted down in energy by 0.1–0.2 eV as a function of the number of Au atoms input. When an Au atom contacts an input branch, the molecule π system is transformed, its states shifted in energy, and its component molecular orbitals are spatially deformed. This deformation is available on many locations on the molecular board indicating a good distribution of the quantum information concerning the status of the inputs over the molecule, in our experiment this information is measured at only one location, that is, the output naphthyl branch. As presented in Figure 4, this change in the spatial distribution of the frontier molecular orbitals

was observed by imaging the HOMO, HOMO-1, and LUMO contents of the ground and first excited states, and by recording constant-current dI/dV maps at their corresponding energies.

CONCLUSIONS

In a QHC designed molecule, a logic operation is performed without clustering qubits in the molecule. It is also not necessary to bind chemical groups like molecular rectifiers, transistors, or switches to construct a logic gate within one single molecule. The local and classical presence of one or two Au atoms on the inputs branches of a trinaphthylene molecule is producing a quantum transformation on its electronic structure readily accessible to tunnelling spectroscopy measurements on the output branch. A molecule with a different molecular orbital structure will produce a different Boolean truth table depending on the symmetry breaking of its molecular orbitals upon interacting with the Au inputs and on how those molecular orbitals are mixed up to shape the true molecular valence states. This QHC design can be generalized to more complex logic functions embedded in one molecule creating a definitive link between molecular electronics and quantum design. For room temperature applications and packaging, the mapping of such QHC design to surface atomic scale circuits is now under active exploration.¹⁴

EXPERIMENTAL SECTION

Analytically pure trinaphthylene synthesized from 3-trimethylsilylnaphthyl-2-trifluoromethanesulphonate *via* a palladium-catalyzed [2+2+2] trimerization^{15,16} (see Supporting Information) was sublimed by free evaporation in an UHV preparation chamber on a Au(111) surface kept at room temperature. Thereafter the Au(111) sample was cooled down to 5 K. With the evaporation parameters used, coverage under 0.1 monolayer was attained. STM imaging shows molecules adsorbed on Au terraces and at step edges. Single Au atoms were produced by a gentle crash of the W tip apex on the Au(111) surface and manipulated with the STM tip for contact with a single molecule.¹⁷ A typical image of a trinaphthylene molecule with three companion single Au atoms is presented on Figure 2a. Three Au atoms were manipulated in close proximity to a molecule: two for the inputs and one as a reference to verify whether the molecule moves during one Au input operation. Standard $R = 250 \text{ M}\Omega$ low bias voltage tunnelling resistance was used for imaging, and $R = 0.2 \text{ M}\Omega$ was used for single Au atom manipulation in pulling mode. Whenever was necessary, a trinaphthylene molecule was manipulated to bring it to the Au atoms, also in pulling mode, using an $R = 200 \text{ M}\Omega$ junction resistance with a large bias voltage.

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Supporting Information Available: Details of theoretical works and methods, Figures S1–S11. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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