A 16-bit parallel processing in a molecular assembly

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A machine assembly consisting of 17 identical molecules of 2,3,5,6-tetramethyl-1,4-benzoquinone (DRQ) executes 16 instructions at a time. A single DRQ is positioned at the center of a circular ring formed by 16 other DRQs, controlling their operation in parallel through hydrogen-bond channels. Each molecule is a logic machine and generates four instructions by rotating its alkyl groups. A single instruction executed by a scanning tunneling microscope tip on the central molecule can change decisions of 16 machines simultaneously, in four billion (416) ways. This parallel communication represents a significant conceptual advance relative to today’s fastest processors, which execute only one instruction at a time.

A molecular machine is a system that generates physical motion of its components at the atomic level, controlled by an external stimulus (1–10). Several novel nanomachines have been realized over the last two decades by rearranging the constituent atoms of nature’s building blocks, namely proteins (11, 12), DNA (13), and other compounds (14–17). Researchers have sought to increase the number of versatile instructions and generate multiple operations by increasing the complexity of design via diverse assembly routes. However, a machine that can modulate the decisions of other machines or communicate with more than one system at a time has not yet been achieved. A major difficulty in realizing such a machine resides in transferring versatile instructions simultaneously at the molecular level in a well-controlled manner, partly because such machines are beyond the reach of today’s atomic-scale manipulation. Linear connection of machines allows implementation of only one instruction at a time. In contrast, the radial connection of machines originating from a central control would allow parallel communication similar to a synaptic channel, but this configuration has not been explored in reported machines. Construction of a machine to process parallel communication will require an encoded molecular assembler (MA) that will precisely position the operational molecules by weakly interacting bonds and translate multiple instructions.

Recently, we have realized a multilevel switch in 2,3,5,6-tetramethyl-1,4-benzoquinone (duroquinone, DRQ) (Fig. 1A), which generates four logic states (0, 1, 2, and 3) within 7 Å when instructed by a suitable scanning tunneling microscope (STM) pulse.1 Each logic state is associated with particular rotation of alkyl groups, satisfying the requirement of a molecular machine. Here, we report a machine assembly consisting of 17 identical DRQs, wherein a single molecule simultaneously instructs 16 others, in 416 possible ways. This machine is made possible by a supramolecular architecture consisting of a ring of 16 analogous DRQs as execution units (EUs) around a single DRQ as central control unit (CCU). Hydrogen-bond channels originating from the CCU radially connect to the 16 EUs, providing synchronized one-to-many control of their states. Instructions are sent by STM pulse to the CCU, which in turn sends 16 unique instructions simultaneously to the 16 EUs. In this way, one can govern billions of decision-making instructions sets to control logic machines simultaneously. The goal of a nano-CPU is to control the independent operation of multiple machines from a control unit. To demonstrate this ability in principle, we have performed density functional theory (DFT) simulations interfacing eight recently invented nanomachines externally to these 16 logic machines and operated them by CCU. The simulated operation shows that all 24 machines respond simultaneously to a single instruction given to the CCU [see discussion on multiple machine operation in the supporting information (SI) Text and SI Movie 1]. These external machines retain their functionalities even in this greater assembly, demonstrating that our basic 17-DRQ assembly can function as a nano-parallel processing unit in addition to its parallel communication capabilities.

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1DRQ alkyls rotate like machines with change in logic states 0 → 1 (120°), 1 → 2 (60°), and 2 → 3 (60°). DRQ single molecule demonstrates double negative differential resistance (DNR) peaks, which creates four different states; two neutral (state 0 and state 2) and two negatively charged either by one (state 1) or by two electrons (state 3). These multiple states of quinones are well known since long time. The previous reports can be found in ref. 18. For detailed RAM, ROM operations of DRQ, see ref. 19. The structural details and STM images of the four states can be found in ref. 20. Similar to DRQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (or DDQ) switches between any four conformers in ~1 μs and remembers a state for ~8 min in an isolated form. Four states in quinones are also confirmed by cyclic voltammetry measurements and simultaneous electronic and optical studies (21). The DRQ is deposited on a reconstructed Au(111) substrate by using a single-crystal gold (99.99% ± 5 Å) substrate reconstructed by annealing the crystal at 700 K for 30 min, followed by Ar sputtering for 30 min (the cycle was repeated five to six times). The DRQ was evaporated from a K-cell at a 100-K substrate temperature in an ultrahigh vacuum STM (10−8 torr) by thermal evaporation from a source kept at 383 K (the melting point for DRQ is 383 K) with an exposure of 15 min.

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We have constructed the machine assembly using 17 identical, randomly distributed DRQs, on an Au(111) surface, deposited in an ultrahigh vacuum (UHV) STM chamber at 77 K.\(^2\) The approaching paths of the DRQs were monitored within \(5 \times 5 \text{ nm}^2\) by scanning at \(-0.6 \text{ V}\) at an interval of 30 sec where the number of participating DRQs was varied from 1 to 21. For “magic” numbers of participating DRQs (4, 6, 8, 12, 16), the motions gradually attenuated into a circular or horseshoe-like semicircular ring. For other numbers of participants between 4 and 21, we did not observe any self-convergence from random initial distributions of DRQs (Fig. 1 B and D). The magic assemblies arise from geometric constraints: 4 DRQs form a square; 6 form a hexagon, whereas odd numbers of participants favor random-chain formation. For 8, 12, and 16 participants, formation of a semicircle with an opening in the circumference is observed (Fig. 1 A and C). Interestingly, for 16 participants, when an additional DRQ is inserted through this opening into the center of semicircle (Fig. 1B), within a span of \(\sim 10\) sec the inserted DRQ reaches the center and completes the circle as a molecular assemblers (Fig. 1 A–C). The molecular compositions of all architectures were confirmed by comparing theoretical STM images generated from the appropriately oriented molecular assembly on Au (Fig. 1C).

The supramolecular assembly configures itself to integrate more DRQs in a characteristic way (Fig. 1D). Equivalent molecular structures generated from computed STM images show that the ensemble with six DRQs remains in a flat configuration (benzene plane at \(7^\circ\) with Au). When eight or more DRQs are brought within the \(5 \times 5 \text{ nm}^2\) area, the assembly switches from flat to edge-on configuration (molecular plane at \(70^\circ\) with Au) and the diameter increases from 1.6 nm to 2.2 nm. As the number of participants approaches 16, the diameter of the assembly saturates at \(\sim 2.5\) nm (Fig. 1C). This nearly constant diameter for assemblies between 8 and 16 results from the necessity of minimizing angular momentum for the integrity of the assembly (deciding relation is \(2\pi r \sim kL\), where \(r\) is the radius of the ring, \(L\) is the width of the molecule, and \(k\) is the number of molecules). Notably, the nearly constant inner periphery of the semicircular ring corresponds to a single DRQ area, providing architectures with a virtual control center, \(V\) (Fig. 1C).

To keep the constant radius observed in larger assemblies, the DRQs are lifted up to accommodate more participants (lift-up process in SI Text and Fig. 5). DFT computations show that in the flat configuration (0.68 nm \(\times\) 0.71 nm, height 0.18 nm), the dipolar potential has continuous rotational symmetry around the dipolar axis, and there is no interaction between neighbors.\(^1\) In the edge-on configuration (0.18 nm \(\times\) 0.71 nm, height 0.68 nm), inner alkyls are coupled with neighbors and the outer alkyls are free to rotate because the hydrogen bonds are localized only within the inner alkyls (see localization of hydrogen bond in SI Text). Because the freedom of functional groups inside of each molecule is restricted in two different ways, each EU functions as two independent functional moieties of \(\sim 3\) Å each.

When an additional flat DRQ is inserted inside of the semicircle made by 16 participants, the inserted DRQ moves to the center automatically and forms hydrogen bonds with the peripheral DRQs along the O-O axis (Fig. 2A). During insertion, oxygen is always facing the opening and the O-O axis does not intersect with the semicircular pattern. The radial forces generated by the hydrogen bonds reconstruct the semicircular structure into a circular one. A higher density of hydrogen bonds along the O-O axis in the final architecture is the signature of this reconstruction (Fig. 2A, marked by arrow). The hydrogen-bond network between 16 inner peripheral oxygen atoms and the central DRQ forms the communication channels (PCs), shown by green channels in Fig. 2A. A supramolecular architecture has a typical bond length between H and another electronegative atom and a closely associated angle beyond which H bond network in the architecture is feasible. In this assembly, this cut-off bond length is \(\sim 0.3\) nm, and the associated threshold bond angle is 36°. As this network is formed, all 18 inner oxygens arrange in a negative isopotential ring while keeping the 16 outer oxygen atoms isolated (Fig. 2B; see locking of architecture in SI Text). The hydrogen-bond network prevents the peripheral inner alkyls from rotating freely, whereas the outer alkyls, which do not contribute to the bonding network, rotate freely, enabling the EUs to switch among four states (Fig. 2A and B; and see SI Movie 2).\(^2\) The functional independence of inter-DRQ coupling is further evident in the two isolated hydrogen-bond networks of inner and outer alkyls (blue nets in Fig. 2A). Consequently, the supramolecular structure has a central control unit (CCU) that can communicate simultaneously with all 16 outer DRQs (EUs) through hydrogen-bond channels (PCs). In SI Movie 4, the contrast of particular 16 bright spots blinks continuously as logical states change, which points to the conclusion that 16 bright spots contain electronically independent structures.

Fig. 2C shows a 3D relative charge density (RCD) generated by DFT calculations of the complete architecture, showing the

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Footnotes:
1. The minimum energy structure and conformational search for the single molecule, dimer, linear, and circular chains, orientation of the molecules on a gold surface, and electronic properties were studied following ab initio Hartree-Fock and DFT computation at the B3LYP level with a 6-311G** basis set. The repulsion during architecture formation is modeled by combining an exponential repulsion with an attractive dispersion interaction (105). \(E_{\text{underweak}} = \sum_{i<j} \alpha \exp(0.005R_iJ^2) - 1.258J^2 \quad \text{where} \quad R_iJ = r_iJ \quad \text{and} \quad k\). The parameters are as follows: \(\alpha\) and \(k\) are the van der Waals radii for the atoms, epsilon (\(\epsilon\)) determines the depth of the attractive potential energy well, and \(r_iJ\) is the actual distance between the atoms. At short distances, the above equation favors the repulsive interaction over a dispersion attraction. To compensate for this fav over short distances (\(r_iJ < 3.8\) Å), the term \(E_{\text{underweak}}\) is replaced with \(E_{\text{underweak}} = 0.136/2 \sum_{i} \alpha \exp(-r_iJ)\). The architecture minimization is repeated until the simulation converges into well observed architecture.

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SI Text

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Fig. 2. Fundamentals of the architecture. (A) Molecular model of the architecture inside its van der Waals sphere (white color) showing three divisions: CCU, PC, and EU. Three kinds of hydrogen-bond communication channels are visualized: green lines connect 16 internal oxygen atoms of DRQ and CCU, orange lines connect external oxygen with CCU, and blue lines are the intermolecular coupling between EU DRQs (see SI Fig. 6 and SI Movie 2). Here, bond length is set at 7.4 Å and angle at 56°. (B) The iso-potential surfaces divide the architecture into two parts: green denotes positive potential and violet denotes negative potential. The central green area is the isolated potential island of control region C, and the outer violet clusters are the execution region E. In Inset, the dotted circle denotes inner alkyls, with an arrow pointing to the schematic of alkyl–alkyl coupling with two O–O connecting axes \(Y^--Y^+\) and \(X^--X^+\) making an angle \(\theta\) at \(V\). (C) Relative charge density (RCD) of the architecture as viewed from top (T) and bottom (B) (see SI Movie 3 for views from all directions). (D) Schematic of RCD features: top (T), middle (S), bottom (B) layers of iso-RCD disk when viewed horizontally. Two columns C and E are observed when viewed vertically. (E) The experimental scheme for STM pulse application on CCU (C) for control and on EUs (E) for read/write.
distribution of electron-density channels connecting different atoms (20). The side view shows an $\sim$2-Å-wide, negatively charged layer (S) sandwiched between 3-Å-wide top and bottom layers (T and B) of positive charge-density distribution (for views from all directions, see the 3D RCD view in SI Movie 3). The CCU modulates the bottom inner alkyls (B) to write the instructions for EUs, while bits on the EUs are registered by rotation of the outer alkyls at the top layer (T), as is evident in the RCD profile (Fig. 2 C and D). Additionally, Fig. 2 C and D shows two isolated circular regions from the top view, one with a diameter of 18 Å (C) where CCU operation takes place and another with diameter 18–21 Å (E) where EU operation takes place. The coexistence of three isolated layers from top to bottom (T, S, and B) and two functional divisions (C and E) allows the architecture to execute parallel processing with multiple functionalities (Fig. 2D). When a bit is written on the outer oxygen of an EU, it stores 1.2%, 2.0%, 1.0%, and 2.5% more negative charge than its counterpart oxygen for 0, 1, 2, and 3 states, respectively; neutral DRQ oxygen shares 33% of total electronic charge. As a result, the central isopotential disk S and central division C containing the CCU are not affected. The change in relative charge pushes EUs radially inward or outward by 0.2, −0.1, and 0.3 nm to register 1, 2, and 3 bits locally while maintaining the integrity of the architecture (negative sign denotes motion toward CCU).

Fixing the STM tip on the outer oxygen atoms of the EUs using the point-contact method, 1-μs pulses were applied to write/erase four logic states 0 (−0.7 V), 1 (1.3 V), 2 (1.5 V), and 3 (1.7 V) (Fig. 2E). The states are read by measuring conductances at 0.2 V. Writing any one among 0, 1, 2, and 3 to each of the 16 EUs produces a 16-bit instruction array; nearly 200 dissimilar arrays have been registered for four given CCU states. For a defined array (e.g., 3012032300210322) switching the CCU (from 2 to 3, for example) by applying a suitable pulse changes electron density at distinct atomic sites in the CCU. Because CCU oxygen atoms are coupled to the inner isopotential oxygen ring, the oxygen ring’s overall charge distribution changes significantly, along with the strength of the hydrogen-bond PCs. To reach equilibrium, certain EUs change their conformation permanently; an external pulse can no longer change their state. Consequently, these bits of the instruction array are fixed, whereas the remaining autonomous bits can still be governed by instructions given by STM pulse. Thus, writing bits to the EUs stores bits locally without changing the state of the CCU.

Once architecture is determined, the relative 3D spatial distribution of relative charge density is calculated by DFT, using numerical orbitals double zeta potentials (DZP), with local density approximation (LDA-PZ) and mesh cut-off at 150 Ry. Strict convergence of Hamiltonian at $10^{-5}$ critical limit was employed during computation.

We fix the STM tip as suggested in ref. 22 and then the point-contact measurements as suggested in ref. 23.
preserves their states unless the CCU instructs them to switch into a new state.

Using these properties, particular instructions can be selectively inserted in the 16-bit signal array by applying a single STM pulse to the CCU as demonstrated in Fig. 3. Four particular instruction arrays were written on EUs for CCU bits 0, 1, 2, and 3, and corresponding changes in the STM images were recorded. These changes were reproduced in the computed local density of states (LDOS) profiles by considering four DRO conformers, generating the equivalent molecular structure of the whole architecture during machine operation. This allows the RCD to be computed, revealing the spatial modulation of electron-density channels during real-time operation. Changes in the hydrogen-bond network during operation are manifested in the tube-like electron-density channels, which traverse across TSB layers and CE divisions (for two-dimensional representation, see Fig. 2 C and D and the three-dimensional view presented in the SI Movie 3) in four distinct ways. Top and side views of the RCD provide direct evidence that the electron-density channels are continuously reconstructed during operation. However, out of four billion choices statistically, we found regeneration of four typical dynamics; snapshots of iso-density channels are shown in Fig. 3 Right.

The selective and parallel modulation of multiple decisions on EUs by a single pulsed instruction to the CCU is demonstrated in Fig. 4. Specifically, a particular array is changed by switching the CCU from state 2 to 0, 1, or 3; after the 2 → 3 transition, CCU is switched back to state 2. A single instruction to the CCU generates 16 particular instructions to the EUs, instructing some to function independently and fixing others to a particular state. All 16 EUs can be permanently fixed by the X → 3 transition (X = 0, 1, 2, or 3); alternately, all 16 can be instructed to operate freely by the X → 2 transition (Fig. 4C). These are the two limiting cases for this unique 16-bit parallel processing. For an advanced application, we have written 40 different random 16-bit instruction sequences on the EUs and simultaneously changed the CCU codes (Fig. 4; and see details in SI Movie 3). From this operation, we have constructed a truth table for the machine. Total number of 16-bit array is halved if C2 mirror symmetry is considered based on H bond network. However, for practical application, we consider that all ring molecules are distinguishable.

When the CCU is switched to the neutral state (0), the 0 state is permanently imposed on the four EUs nearest to the CCU oxygen atoms, irrespective of the initial 16-bit array. The DFT calculations suggest that a stronger network between the CCU and these four EUs fixes them in the same state (0) as the CCU (Fig. 3A). It is possible to write any of the four different states independently on the remaining 12 EUs, which could generate 4^12 instruction arrays.

When the CCU is switched to state 1, it permanently encodes state 2 in every second pair of EUs [X → 2 (X = 0, 1, 2, 3)]; this state corresponds to the neutral DRO (Fig. 4B). The DFT calculations suggest that charge is distributed in iso-DOS clusters at four symmetric positions on the ring. The resulting configuration has eight EUs coupled to the CCU and eight independent EUs. The eight independent EUs can generate 4^8 independent decision sets encoded with state 2. STM images of all six arrays show iso-LDOS clusters at these positions (Fig. 4B).

When the CCU is switched to state 2, the central DRO relaxes to another neutral conformation and the dipole moment is reduced from 1.8D to 0.62D. The DFT calculations reveal a homogeneous RCD distribution (Fig. 3C), and the decoupled EUs are free to switch among any of the four logic states, as shown by the isolated LDOS clusters in the STM image. Therefore, in principle, all 16 bits, comprising 4^16 decision sets, could be set free from any CCU control.

When the CCU is switched to state 3 (doubly reduced state), the electron density of the inner ring increases significantly. DFT calculations show the PCs reorienting to a new equilibrium with one to two correspondences. Each pair of adjacent EUs is strongly coupled and acquires the same logic state, choosing the smaller of the two initial states. Therefore, irrespective of the initial 16-bit array, eight pairs of decisions are permanently fixed. Six of the 4^6 possible arrays are shown in Fig. 4D. The associated truth table is summarized in circular form; however, a classical presentation is available in SI Table 1. All 16 ring molecules are assigned a rank from 0 to 15 to construct a 16-bit array instruction. We select a particular molecule as the most significant bit (MSB) and another as the least significant bit (LSB). Therefore, the decision-sets calculated above are distinct, even if the structure is symmetric.

Finally, we note that the negative charge and radial motion of isolated EU oxygen atoms modulate the neighboring electron-density ripples, changing their height and period (20, 24) (Fig. 4). Consequently, every 16-bit array has a characteristic signature extending around the machine. This provides further evidence that we have built an assembly wherein we instruct 1 molecule at the center and 16 molecules in the ring are instructed at once in a logical way. The concept of simultaneous one-to-many communication could be generalized in building massive supramolecular architecture wherein parallel signal processing would be established.

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