Prospects for Single Molecule Information Processing Devices

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Contributed Paper

Present information technologies use semiconductor devices and magnetic/optical discs; however, they are all foreseen to face fundamental limitations within a decade. Therefore, superseding devices are required for the next paradigm of high-performance information technologies. “Single molecule devices” have been expected to be the most probable candidate; however, they have not been made practical since they were first proposed more than a quarter of a century ago. The major obstacles are the extreme difficulty in accessing a single molecule, and the very complicated electron states of a molecule connected to electrodes. With the advancements in scanning tunneling microscope (STM) and simulation technologies, the design and demonstration of single molecule devices are close to reality. This paper first reviews the architectures suitable for single molecule information processing, in which it is claimed that the performances of information processing is higher, if speed and element number product is larger in almost all architectures. Then, prospects for single molecule devices, including switching devices, wires, diodes, nanotubes, optical devices, storage devices and sensing devices for future information technologies and other advanced applications are described. Four milestones for realizing the peta/exa-floating operations per second (FLOPS) personal molecular supercomputer are proposed. Current status and necessary technologies of the first milestone are described, and necessary technologies for the next three milestones are also discussed.

Keywords—Conducting molecule, high-performance information processing, information processing switching device, information technology, single molecule device.

I. INTRODUCTION

Human beings have made enormous progress in information technology since civilization started several thousand years ago. However, the three elements of information technology—information processing, transmission, and storage—were done almost exclusively on paper, since its invention about 2000 years ago until about 50 years ago, except wireless communication using noroshi or smoke, and calculation using soroban or abacus, as indicated in Table 1.

In the latter half of the 20th century, electronic information technologies started to emerge, and transistor based information processing, semiconductor laser-based information transmission and magnetism based information storage have become dominant and completely changed human life into an “information society.” Optical storage systems and sensors have also contributed to progress in the knowledge and welfare of humanity. Thus, tera (T; $10^{12}$)-floating operations per second (FLOPS) computation is already accomplished, and peta (P; $10^{15}$)-FLOPS computation would be necessitated by 2010, and exa (E; $10^{18}$)-FLOPS computation would be demanded by 2020 [1].

However, present information devices are facing very fundamental physical, chemical and materials limitations in such characteristics as operation speed, density and sensitivity in order to cope with the demands from the information technology. Take the example of information processing switching devices, such as metal–oxide–semiconductor field effect transistors (MOSFETs) [2], [3]. Among dozens of semiconductor devices that have been proposed [4], only MOSFETs survived the harsh competition, with the rare exception of bipolar transistors. The reason behind this
is that MOSFETs meet the fundamental requirements of information processing devices almost perfectly in a very balanced manner, as will be discussed in Section III-C [5]. Furthermore, their performance can be improved by simply reducing their dimensions, which will also be explained in Section III-A. Dozens of “new concept semiconductor devices” have been proposed as candidates to replace MOSFETs; however, their overall performances are not necessarily superior to those of MOSFETs. Therefore, MOSFETs are expected to continue evolving until they reach their ultimate limitations, which will probably be within ten years from now [6], [7], as will also be discussed in Section III.

In order to make possible further progress in information technologies, several information processing nanoscale device ideas were proposed, including quantum devices [8], single electron devices [9] and single molecule devices. Among these candidate devices, single molecule devices would make it possible to realize the most advanced information processing device characteristics and system performances, because of their potential advantages such as nanometer size, high functionality, and mass producibility. They were proposed more than a quarter of a century ago [10]; however, they have not been made practical yet [11], [12]. Two major reasons for this are the following: it is very difficult to access a single molecule, and the electron states of a molecule are very complicated when it is connected to the electrodes, which makes it very difficult to design appropriate molecular structures. In addition, the extremely rapid progress of semiconductor technology had left the direction for molecular electronics almost disregarded by the industry. Recent progresses of scanning probe technology [13] and computer simulation technology [14] have made these two technologies almost mature enough to conquer the obstacles against realization of single molecule devices. At the same time, the fundamental physical, chemical, and material limitations of semiconductor devices forced us to start very serious discussions within the industry for a paradigm shift of information processing technology, and to revisit molecular electronics ideas.

This paper reviews the present status of research on using single molecules for advanced information technologies, placing emphasis on information processing switching devices. The outline of the paper is as follows. In Section II, the architectures suitable for single molecule information processing are described, in which it is claimed that the performances of information processing are higher, if the product of speed and number of elements is larger, almost regardless of architectures. Section III outlines the history and foreseeable limitations of present information processing devices, MOSFETs. It is predicted that the limitation would be within 10–15 years, and that superseding device is definitely needed. Section IV describes why single molecule devices would be considered to be the most suitable devices for realizing high-performance information processing, and summarizes switching devices for information processing, which are expected to supersede MOSFETs beyond their limitations. Other applications of single molecule devices for advanced information technologies are listed in Section V, including molecular wires, diodes, light-emitting devices for display and information transmission, which might replace semiconductor light-emitting diodes and lasers, high-density storage devices for information storage, which could overcome the limitations of magnetic disks, and single molecule detection devices for highly sensitive sensors. Sections VI–VIII describe four milestones for realizing single molecule devices for the future information processing, and present status of technology development. Several indispensable technologies for the final destination are listed.

II. POSSIBLE ARCHITECTURES FOR SINGLE MOLECULE INFORMATION PROCESSING SYSTEMS

Possible architectures suitable for molecular information processing systems are briefly discussed in this section. Almost all the present computer architectures rely on the von Neumann architecture [15], [16], defined by a “stored program” structure, in which memory and logic circuits play the key role. Table 2 summarizes currently investigated as well as practically applied computer architectures, including von Neumann and non-von Neumann architectures, together with the devices suitable for realizing the highest performances. Almost all of the present computers utilize MOSFETs regardless of architecture, except for neural network architecture [17], [18], which uses neuro devices [19], [20], dynamic architecture, which uses field programmable gate array (FPGA), and quantum computing [21], [22] which uses nuclear magnetic resonance (NMR) and quite recently, solid state quantum bit (qubit) was successfully demonstrated for the first time [23]. Other architectures such as quantum cellular automata [24], might also be attractive from the single molecule device point of view, because it only employs connections between the nearest neighbors, which was already partly demonstrated using nano particles and connecting molecules [25], DNA computing [26] might

<table>
<thead>
<tr>
<th>ARCHITECTURE</th>
<th>DEVICE</th>
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<tbody>
<tr>
<td>von Neumann type</td>
<td>MOSFET</td>
</tr>
<tr>
<td>non-von Neumann type</td>
<td>cellular automaton</td>
</tr>
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<td></td>
<td>neural network</td>
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<td>data flow</td>
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<td>dynamic architecture</td>
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<td>quantum computing</td>
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The performances of a computer $P$ is roughly approximated by the following equation [16] independent of architecture, in which $k$ is a constant, $N$ is number of elements, and $F$ is operation frequency.

$$P = k \times N \times F.$$  \hspace{30mm} (1)

Equation (1) indicates that the performance of a computer is higher if the number of elements is larger and the operation speed is faster. Here, the guiding principle is “the greater the number the better, the faster the better.” Therefore, single molecule devices would make possible several orders of magnitude higher performance information processing because of their potential in high switching speed. Considering that number of devices in a system can be made larger in the molecular system, the performance would be made much higher, according to (1).

Quantum computing architecture [21], [22] might also be made possible by employing the coherent transport principles in a molecule to be discussed in Sections V-D and VII-A2. Another topic is the fault-tolerant scheme [27], in which a defective part of the system is merely detoured around by software/hardware rearrangements. This system is practically based on von Neumann architecture and could also be applied to current computer systems using MOSFETs, although the cost issues due to the increase in hardware and software resources are not yet solved. A molecular system should be able to make the best use of the advantages of this scheme, because of their potentially redundant nature.

In 20 years, other architectures, currently in research status or even pre-evaluation status, might be brought into the mainstream of information processing. Still, the potential high switching speed and high density integration of single molecule devices would bring the information processing system to the highest performances and would contribute to the human welfare.

III. LIMITATIONS OF PRESENT INFORMATION PROCESSING DEVICES

The reason why MOSFETs have solely been used in almost all the architectures described in Section II is that they fulfill the requirements of information processing devices to be discussed in Section III-C nearly ideally. However, as mentioned above, the limitations of present device technologies must be overcome by superseding devices for further advancement of information technologies. This section first describes the limitations of present information processing devices, placing an emphasis on MOSFETs. Then, the necessary characteristics for future information processing devices are discussed. Finally, microminiaturization trend of magnetic disks is briefly mentioned as the representing device for information storage.

A. Scaling Principle of MOSFETs

Today’s highly advanced information processing instruments depend solely on innovations in integrated circuits (ICs) [28], [29], which consists mainly of MOSFETs [2], [3]. For example, the advanced personal computers used to write articles, calculate equations, and transmit information through the Internet rely solely on ICs for their high performance. The innovation of IC technologies started in 1970, and the integration had quadrupled, as well as the minimum dimensions of the transistors had been reduced by a factor of 0.7 every three years since then, as shown in Fig. 1 [4]. Consequently, the integration of ICs has increased almost one million times in about 30 years. This indicates that the performance of ICs has also quadrupled every three years. In other words, it takes only five years to improve the performance of ICs by one order of magnitude.

Fig. 2 schematically depicts cross section of present complementary metal–oxide–semiconductor (CMOS) FETs with multilayered interconnection wiring [30]. Today, the role of interconnects have become more and more important; however, MOSFETs still play the main role in ICs for information processing. The processing steps to fabricate CMOS ICs, corresponding to Fig. 2, are shown in Table 3 [30]. It usually takes at least several weeks to finish producing CMOS ICs through these process steps, even by using the most advanced fabrication equipments. How MOSFETs have been made smaller between 1980 and 2000, and will be made smaller by 2020 is schematically shown in Fig. 3. For example, the gate length is made shorter by about one order of magnitude in 20 years, though the operation principle is the same: control the current flow between drain and source by the potential applied to the gate [2], [3]. The basic principle behind this innovation is called the “scaling principle” [31], in which the lateral as well as vertical dimensions are shrunk by a factor of $k$, while the impurity concentration is increased by a factor of $k$, resulting in an improvement of switching speed by a factor of $k^2$ and switching energy by a factor of $k^3$, as indicated in Table 4. Here, the guiding principle is “the smaller the better.” Most major industries have
experienced this logarithmic advancement, called a “logistic curve” [32], in which the logarithmic rapid growth generally lasted for about 30–50 years.

B. Limitations of MOSFET Scaling

Despite these enormous advancements, the progress will likely cease sometime early in the 21st century, when device, technology, material, and physical limitations will be reached [33]. There are various predictions about reaching the limitations of MOSFET innovation; some are optimistic [30], [33] and others are pessimistic [6], [7]. The major obstacles to further scaling of MOSFETs are as follows [4].

1) Semiconductor Limitation: The built-in voltage of p–n junctions cannot be scaled to reduce the depletion region width;

2) Dielectric Limitation: Bandgap energy of insulators cannot be scaled to cope with the high electric fields or quantum tunneling;

3) Conductor Limitation: The current capacity of metals cannot be scaled to handle the increase in current density;

4) Statistical Error Limitation: A fewer number of impurities causes increase of variation due to the $\sqrt{N}/N$ statistical errors;

5) Mobility Limitation: The carrier mobility in the channel region saturates and cannot be scaled.
Table 4
The Scaling Principle by Which MOSFET Sizes are Shrunk. The Horizontal as Well as Vertical Dimensions are Shrunk by a Factor of $k$, While the Impurity Concentration is Increased by a Factor of $k^3$. They Result in the Following Improvements in Performances: Switching Speed is Increased by a Factor of $k^3$, and the Switching Energy is Reduced by a Factor of $k^3$.

"SCALING PRINCIPLE"

1. DECREASE LENGTH AND THICKNESS
2. INCREASE CONCENTRATION
3. KEEP FIELD STRENGTH

DELAY : $1/k$
POWER CONSUMPTION : $1/k^2$
PATTERN DELAY PRODUCT : $1/k^3$

6) Parasitic Parameter Limitations: Parasitic parameters such as capacitance and resistance of MOSFETs cannot be neglected any more. Combined, these limitations will prevent MOSFETs from being scaled down below around 100 nm, which might be reached in ten years from now. Even if the most optimistic prediction holds true, these limitations will prevent further scaling within 15 years. Therefore, superseding devices are required for information processing technologies to continue advancing in the 21st century.

C. Necessary Characteristics for Superseding Information Processing Devices

Here, the necessary characteristics for new information processing devices will be considered, and the possible reasons for the dominance of MOSFETs are discussed. The five most essential characteristics for information processing devices are as follows [4].

1) I/O Signal Balance: the output signal of one device should be able to drive the next device directly.
2) I/O Isolation: more than three terminals are required to separate the input and output signals of a device.
3) Fast Operation Speed: to cause a paradigm shift, the switching speed should be faster than present device by orders of magnitude, as will be described in Section IV-A.
4) Dense Integration: the device integration density should be higher than that of the present devices to avoid possible signal transmission delays, and to proportionally meet the improvements in the switching speed.
5) Fabricability: the device should be fabricated by mature technologies.

The reason why MOSFETs have become so dominant in information processing is that they have an almost ideal balance of these five characteristics. While other devices may be superior in one or two ways, their total performances are far from comparable. Of course, other factors such as noise immunity, reliability, and power consumption have to be taken into consideration in integrated circuits, but these five characteristics are the essential ones, and should thus be given first priority when evaluating new device concepts.

D. Miniaturizing Limitation of Information Storage Devices: Magnetic Disks

Other quite important devices that support the advanced information technology are information storage devices. Here, the progresses and limitations of magnetic disks are briefly stated. Magnetic disks have more than 40 years of history, and the bit area has been reduced by an annual rate of 30%–60% until quite recently, as shown in Fig. 4. In the same figure, innovation of DRAM memory cell area is also plotted. It is quite notable that bit areas of these two devices, operating under quite different principles, are quite similar. It is also quite notable that the input–output (I/O) data rate of magnetic disks are made higher, and reaching more than 20 MB/s these days, and would reach 1–100 GB/s by 2020. Several factors that limit further increase of bit density are considered, and ultimate bit density is foreseen to be around 40–100 Gb/in$^2$ [34], [35], thus, innovative storage devices under a new paradigm are also unquestionably required, and in the same line, microminiaturization of magnetic disks is also making progress at an enormous rate [36].

IV. SINGLE MOLECULE INFORMATION PROCESSING DEVICES

A. Why Atom/Molecule Devices for the Next Paradigm?

As discussed in the previous section, present information processing devices are facing fundamental limitations arising from their physical, chemical, and materials properties. Therefore, innovation is definitely needed for the next
paradigm shift of information processing devices. Which direction should we take? There is a proverb in Japan, pronounced “On-ko-chi-shin,” which means that “look back at history and you will know what will happen in the future.”

Fig. 5 depicts the switching speed and integration density relationship of historical information processing devices, showing that human beings started electronic information processing with relays [5]. These were replaced by vacuum tubes and transistors. Now, integrated circuits dominate the information processing devices. The figure clearly indicates that orders of magnitude improvement in such characteristics as switching speed and integration density are essential to bring about a paradigm shift in information processing devices. This implies that the information processing devices under the next paradigm will have switching speeds of more than 1 THz and will integrate more than $10^{10}$ devices/mm$^2$, which indicates that the superseding devices should be nanometer scale. Therefore, atom/molecule size device ideas have been proposed for the next paradigm [37].

If all information processing devices were fabricated using single molecule technology, not only would the switching speed and integration density of the devices be improved by orders of magnitude, but also the total energy consumed by the integrated system would be reduced by orders of magnitude. In addition, the total amount of materials and energy necessary to fabricate the system would be reduced enormously because perhaps $10^{20}$ molecular devices can be synthesized in a test tube at one time. Only an order of $10^{10}$ molecules would be needed to construct an advanced information processing system. Thus, single molecule based information system would satisfy the requirements for the high-performance information processing and realize ecology-friendly fabrication.

B. Initial Ideas for Single Molecule Devices

The first single molecule device idea, the “molecular diode,” was theoretically proposed by Aviram and Ratner in 1974 [10]. This was followed by an experimental demonstration of a “molecular photodiode” by Fujihira et al. in 1976 [38], [39]. The “molecular device” idea, then, was proposed by Carter in 1980 [11], which stimulated academia to enter a new era of devices, and several “molecular device” ideas have been proposed and have attracted the attention of many scientists.

These devices, however, have not been made practical for almost two decades, primarily because there was no way to access a single molecule before the invention of the scanning tunneling microscope (STM) [13]. In addition, many of the devices were proposed simply because they might demonstrate very interesting switching characteristics from the fundamental research point of view, though not necessarily from the practical application point of view. Because of the harsh competition among semiconductor devices for survival [4], and the enormous improvement in the performance of MOSFETs [6], the molecular device ideas were only discussed within academia, and they did not attract the attention of the information processing device engineers; therefore, this first wave gradually faded away [12].

C. Single Molecule Device Ideas Revisited—Three Terminal Devices

The improvement in the performance of STM [40], [41] has made it almost possible to access a single molecule. In addition, the limitations of MOSFETs are beginning to be discussed much more seriously than before. Therefore, single molecule device ideas have been revisited, and many small workshops and symposia in large society meetings have been held since the mid 1990s. Several examples are listed in [42]–[48]. Since three terminals are essential for information processing devices, as discussed in Section III-C, the following sections first summarize three terminal switching device ideas, classified according to different switching mechanisms: conformational change, single electron transfer, internal mechanical movement, and potential modulation.

1) Switching Using Conformational Change of a Molecule: This “classical” molecular device idea was mostly based on the structural change of the molecule, because chemists played a central role in the initial stages of the development of molecular device ideas. Conformational changes, such as cis-trans transition, were used as the major switching principle, and some of the typical examples are described in [11], [12], [42]–[45]. Such devices would not switch at more than several kilohertz, because, as is usually the case, the reverse conformational transition is much slower in the molecular system. These nonsymmetrical switching characteristics might be due to the energy differences between the double well system of the two molecular structure states. Present information processing technology requires symmetrical switching device characteristics, because it relies on switching between “1” and “0,” with no predetermined or preferential switching direction. Information processing speed is dominated by the slowest process in the existing architecture, and any slow switching step would lower the total performance of the system.
2) Switching Using Single Electron Transfer Principles: A high-performance single molecule switching device based on single electron transistor (SET) principles was proposed [49]. In the SET structure, the switching frequency $S$ (Hz) is theoretically approximated to be inversely proportional to the square of the size of a quantum dot $L$ (nm) [50]

$$S = \frac{3 \times 10^{14}}{L^2}.$$  

(2)

However, this estimate is too optimistic, although the SET operation speed could reach more than 1 THz if $L$ is reduced to the nm regime, as shown in Fig. 6 [51]. Detailed analysis of the dependence of $S$ on $L$ revealed that (2) should be approximately rewritten as

$$S = \frac{10^{13}}{L^2}.$$  

(3)

Therefore, it is essential that the quantum dot is very small—nanometer in size—to make the SET operate in the terahertz regime [51].

Conventional nanolithography technologies [52]–[54] would not be able to fabricate a quantum dot in the nanometer regime at the accuracy required for ICs with billions of SETs, so the only way to make reproducible device fabrication would be to use molecules. Fig. 7 schematically shows the molecular single electron transistor (MOSES) idea [49], [55]. The figure suggests that, by using conducting molecules for the quantum dot, source, drain and gate electrodes, as well as insulating molecules for the tunnel junctions and the gate insulator, it would be possible to achieve more than 1 terahertz operation of a MOSES. A detailed analysis of the MOSES operation characteristics would permit the precise design of the quantum dot size, the tunneling barrier height and width, the gate insulator specifications, and the electrode characteristics. Thus, the most appropriate structure might not necessarily be the one depicted in Fig. 7, and suitable variations could be taken into consideration. Chemical synthesis of the MOSES molecules should also be a very interesting research and development objective.

Random access memory (RAM) cells, read only memory (ROM) cells, and logic gates could be formulated based on the MOSES structure, and are schematically depicted in Fig. 8. A RAM cell (a) uses three transistor dynamic random access memory (DRAM) scheme; however, four-transistor static RAM (SRAM) scheme can also be applied. Conventional one-transistor one-capacitor memory cell currently used in MOS DRAMs [56] would not be suitable for molecular memories, because of the difficulty in sustaining large capacitance in a molecule. ROM cell (b) stores charge in the gate region of the control transistor. Operation would be more stable if the number of transistors are appropriately increased in the logic gates (c), as in the semiconductor ICs [57]. A complementary SET (CSET), operating like a CMOS transistor, was proposed [58], and the performance was evaluated by simulation. Application of the CSET scheme to memory cells and logic gates would result in more optimal operation characteristics, such as a wider operational margin of a circuit. Similar switching device ideas based on resonant tunneling principles [59] and electric field effects [60] have also been proposed.

3) Switching by Mechanical Movement of an Atom in the Molecule: The atom sized atom relay transistor (ART) was proposed in which the mechanical motion of an atom causes a conductance change, or switching, of an atom wire, as schematically shown in Fig. 9(a) [5]. Electron transport through the atom wire was calculated using a tight binding method, and the results are also shown in Fig. 9(b). The results clearly indicate that the conductance of electrons through the atomic wire is switched according to the position of the switching atom. The switching speed of the ART was simulated using a first principles method, and the switching atom can move at a frequency of more than 30 THz [61] when a silicon atom is used as the switching atom. If a carbon atom is used as the switching atom, the switching speed would far exceed 100 THz, allowing the ART to operate at a very high speed. The switching characteristics

![Fig. 6](image-url) Simulated single electron transistor operation speed dependence on the quantum dot size. It is predicted that the SET operation speed should be more than terahertz, if the quantum dot size is reduced to a nm regime. $d_i$: Tunneling gap distance. $eV_{op}$: Operation voltage. $f_0$: Barrier height.

![Fig. 7](image-url) Schematic figure of the molecular single electron transistor (MOSES) idea: quantum dot is made up of conducting molecule, which is connected to source and drain electrode molecules sandwiched with two tunneling junctions, and gate electrode connected via gate insulator.
were also predicted by simulation, and it was shown that a displacement of the switching atom by only one diameter would change the conductance of the atom wire by orders of magnitude [62]. A molecular version of ART, supra molecular atom relay transistor (SMART) was proposed, and the schematic structure is shown in Fig. 10 [63]. The rotation of the molecule allows the conductance of the atom wire to change according to the position of the molecule. The rotation speed should far exceed the terahertz regime, and the switching characteristics should be highly superior. Therefore, molecular scale “mechanical electronics” (relays) might be reviving after 50 years of absence from the main current of information processing [5]. Memory cells and logic gates have also been proposed, and a 1000 times

Fig. 8  Schematic figure of (a) random access memory (RAM), (b) read only memory (ROM), and (c) logic gates using the MOSES concept. A RAM cell uses three transistor dynamic RAM (DRAM) scheme; however, four-transistor static RAM (SRAM) scheme can also be applied. ROM cell stores charge in the gate region of the control transistor. Operation would be more stable if the number of transistors are appropriately increased in the logic gates, as in the semiconductor ICs.
4) Switching Based on Potential Modulation in the Molecule: Another switching principle relies on potential modulation in a molecule, in which the impedance of the molecule should vary with molecular structure [67]. This scheme was designed to avoid the possible long delay and severe Joule heating caused by the high resistance of molecules. Simulation results indicate that the electronic structure in a three-terminal molecule changes according to the potential applied from one terminal. Since the propagation of potential within a molecule should be very fast, the switching speed would be extremely fast. There remain several questions to be answered. For example, potential injection and detection would be necessary in this potential modulation scheme, which might require carrier transport, as in conventional carrier transport type devices. Despite these unanswered questions, this scheme would also lead to a promising candidate for a single molecule information processing device.

5) Evaluation of the Single Molecule Switching Device Ideas for Information Processing: The single molecule switching device ideas for advanced information processing were evaluated based on the necessary characteristics listed in Section III-C. Table 5 summarizes the evaluation results, in which it is indicated that single molecule switching devices (SMSD), including the mechanical switching devices, single electron switching devices, and potential modulation scheme devices, would be the most appropriate devices for the next paradigm of information processing [5]. Thus, a P-FLOPS personal supercomputer could be constructed based on these single molecule devices. By operating in parallel, the SMSDs should formulate the basis for E-FLOPS high-performance computing. Challenges would still continue to design very fast switching devices that mutually fulfill the necessary characteristics for information processing devices.
Table 5
Evaluation Results of the Proposed Information Processing Devices Based on the Necessary Characteristics Listed in Section III-C. Single Molecule Switching Devices Satisfy the Conditions Most Appropriately Among the Candidate Devices, Except for Fabricability

<table>
<thead>
<tr>
<th>MOS FET</th>
<th>QUANTUM DEVICE</th>
<th>SET</th>
<th>MOLECULAR DEVICE</th>
<th>SMSD</th>
</tr>
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<tbody>
<tr>
<td>I/O BALANCE</td>
<td>○</td>
<td>△</td>
<td>○</td>
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<tr>
<td>I/O ISOLATION</td>
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<tr>
<td>SPEED</td>
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<tr>
<td>INTEGRATION</td>
<td>○</td>
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<tr>
<td>FABRICABILITY</td>
<td>○</td>
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</table>

○ EXCELLENT  △ GOOD  ◐ FAIR
SMDS: Single Molecule Switching Device

V. OTHER POSSIBLE SINGLE MOLECULE DEVICES

This section reviews other possible single molecule devices than three terminal devices for advanced information technologies, such as molecular wires, diodes, magnetic molecules, carbon nanotubes, optical devices including light detection, and light emission single molecule devices for high efficiency display, single molecule data storage devices for ultrahigh-density storage system, and single molecule sensor devices for single molecule detection. The very vast spread of possible applications of the single molecule devices suggest a material paradigm shift from semiconductors and magnetic/optical materials to carbon-based molecules within the next several decades, as indicated in Table 1.

A. Molecular Wires

This section describes several molecular wires, including conjugated oligomers, porphyrins, and dangling bond wires, which would be used in wiring of information devices as well as in the demonstration of a conductance of a molecular wire, “the first milestone,” to be described in Section VII. Several necessary characteristics for the molecular wire are also listed in Section VII-B.

1) Conjugated Oligomers: Conjugated oligomers with a very controlled length have been synthesized, as schematically shown in Fig. 12 [68]–[70]. Generally, their main chains consist of pyrrole, benzene, and thiophene rings and double/triple carbon–carbon bonds to provide π electrons. However, these molecules are close to being insulators, with a 2–3-eV bandgap energy. Therefore, the conduction characteristics might be those predicted by theory as will be discussed in Section VII-A. Those molecules might not be suitable for conventional current injection-type single molecule devices, because the high resistance would cause very severe resistance–capacitance (RC) delay and joule heat generation. Consequently, potential modulation type devices [67] would be the most appropriate device structure for these molecules. The question still remains whether they are mechanically very rigid and straight, and accurate structural prediction is essential from the molecular design point of view. A molecular “enamel wire,” in which insulators are placed around conducting center, would be made possible by those molecules. This is because there remains enough room for attaching side chains for isolating the main body from other molecules, as well as for adding doping substances to generate carriers within the molecule, which would make these molecules good conductors, which will also be discussed in Section VII-C.

Several ideas for low resistance molecules have been proposed, one of which is a zero bandgap [the difference between the lowest unoccupied molecular orbital (LUMO)—highest occupied molecular orbital (HOMO) energy levels] molecule [71], [72]. The guiding principle is to use monomers of reduced aromaticity as a base monomer and to connect several monomers to form oligomers, and a zero bandgap molecule should be formed. Currently, a monomer was successfully synthesized, with an oxidation–reduction energy (LUMO–HOMO gap) of about 0.6 eV, which is the smallest for single molecular unit so far reported, as shown in Fig. 13. Extrapolating from the measured curve, an oligomer with five such monomers should exhibit zero bandgap molecular characteristics. The stability of a zero bandgap molecule in a conventional environment has to be ascertained.

2) Porphyrins: Another possible candidate molecule is porphyrin, a derivative of the light harvesting molecules [73]. Various modified structures have been reported [74], [75], and they are very rigid, thermally stable, and the length can easily measure as long as 10 nm. Typical examples are schematically shown in Fig. 14 [74], in which the tetragonal pyridine-based structure is very rigid, and the
Fig. 13  Schematic structure of a zero bandgap molecule monomer candidates: oxidation-reduction curve measurements indicating a 0.6-eV LUMO–HOMO gap in (b), and suggesting the possibility for zero bandgap.

meta-dibutyl-benzo- part (Bu) attached to the tetragonal part would provide insulating characteristics of the “molecular enamel wire.” In addition, the –N–N– part at the end of the molecule would attach to the gold electrode and function as a “alligator clip.” Moreover, three and four terminal structures have already been designed and synthesized. However, analysis of electronic structures suggests that conventional porphyrin molecules might also have 1–2 eV of bandgap energy [75]. Therefore, it would be necessary to attach donors or acceptors to the molecule to supply carriers to the main body of the molecule, providing the molecule with metallic or semiconductor characteristics. Recently, very long and single-structured porphyrin molecules were synthesized, which extend as long as 100 nm [76], and an optical bandgap of which measures less than 0.6 eV, which is the smallest for molecules with a designed structure so far. These results suggest a very high potential of synthetic chemistry, by which an appropriately designed molecule, both structural and electronic, would be realized with the designed structures and functions.

3) “Dangling Bond Wire” Molecule Formed on Hydrogen Passivated Silicon Surface: Another possible molecule is a “dangling bond wire,” which is formed on hydrogen passivated silicon (100) surfaces [77]. A high voltage or high current is applied from an STM tip to the hydrogen atoms covering the silicon surface, causing them to be released from the surface. A schematic diagram and an STM image of the “dangling bond wire” structures are shown in Fig. 15, in which the white dots represent the locations where the hydrogen atoms were removed [78]. Theoretical considerations using a first principles method [79] indicate that these dangling bond wires should be conductors and that the electronic structures are very confined, so that the dangling bond wire regions may be used as a conducting “molecule.” However, there still remains the basic question of whether isolation between the wire and the substrate can be achieved, though a theoretical work predicts a good isolation in certain cases [80]. Intensive work is still necessary to advance the technology and to develop device structures. Still, a clever combination of the single molecule device ideas and the dangling bond wires could result in high-performance device structures.

B. Diodes

As described previously, molecular diode was first proposed theoretically by Aviram and Ratner [10] in 1974. The basic idea is to control the LUMO–HOMO energy levels in donor–barrier–acceptor structures by a clever design of the molecule. Rectifying current–voltage (I–V) characteristics are expected due to the asymmetric energy levels. Since then several ideas have been proposed, and almost all of them follow this structural design principle. Another notable proposal is a molecular resonant tunneling diode [81]. The basic operation principle is almost the same as the semiconductor resonant tunneling diode fabricated using molecular beam epitaxy (MBE) [82], in which a thin conducting GaAs layer is sandwiched between electrodes separated by two GaAlAs barriers and current flows through the structures when the energy levels coincide with each other, resulting in a negative differential resistance characteristics. The molecular version has quasi-one-dimensional structures and higher peak-to-valley ratio can be expected due to the potentially nondispersive energy levels. However, two terminal devices, even the very fast Esaki tunnel diode, have never been used in a modern complex information processing system as main devices, because of the limitation due to the difficulty in isolating I/O, as pointed out in Section III-C.

C. Magnetic Molecules

Organic ferromagnetic molecules exhibit single spin characteristics, which would have magnetic properties with the smallest possible dimensions, making them potentially applicable not only to information storage devices but also to information processing devices. The first magnetic molecule was theoretically proposed and experimentally demonstrated in 1991 [83], [84], and since then several spin polarized molecules have been synthesized and evaluated [85].

Several spin generation mechanisms have been reported. One is to decompose a molecule, for example, diphenyl-di-azomethane, by irradiating light to release a nitrogen molecule and leave two single spins behind within the molecule.
Another is to use the topology of the molecule, in which a non-Kekule type meta-quino-dimethane molecule leaves two single spins due to the electron resonant conditions. Typical examples of a magnetic molecule are schematically demonstrated in Fig. 16 [86]. Several molecules exhibit a very large spin quantum number, larger than those of conventional ferromagnetic metals [86]. However, a very low temperature is usually necessary to observe the ferromagnetic characteristics of the molecules with the exception of nitronyl-nitroxide molecules. In spite of these limitations, the magnetic molecules should exhibit very attractive characteristics from the single molecule device point of view, and they would possibly be applied to logic devices, memory devices, and sensing devices [87].

D. Carbon Nanotubes

Carbon nanotubes were found in an arc discharge product by Iijima in 1991 [88], and since then enormous numbers of studies have been conducted [89]. Because the size of carbon nanotubes is moderate and individual tubes can be accessed relatively easily, several studies have already been reported on the resistance measurement [90], [91]. Moreover, FET characteristics were demonstrated using carbon nanotube as a channel [92], [93], and the potential distribution along the nanotube of the FET structure was also investigated [94]. Although the current gain is far from comparable to silicon MOSFETs, there is a very good potential
Fig. 16  (a) Schematic demonstration of the principle of the spin generation mechanism within a molecule and (b) typical examples of the magnetic molecules. By forming donor radical, the spins within a molecule arrange to introduce ferromagnetism to the molecule.

for a practical application of nanotubes for use in three terminal information processing devices. Another quite notable demonstration has been reported recently, in which carbide contacts were formed on both ends of single wall carbon nanotubes and were observed by a transmission electron microscope (TEM). The current–voltage (I–V) characteristics of the nanotube was confirmed to be ohmic, and the resistance was on the order of kilohms [95]. Quite interesting characteristics, such as coherent spin transport through a nanotube, are experimentally demonstrated [96]. This result suggests a potential for using nanotubes as a solid-state device for quantum computing, as pointed out in Section II. In addition, magnetic field induced metal-insulator transition was theoretically predicted [97], which suggests the potential of nanotubes to be use in a magnetic information storage systems.

The bandgap energies of carbon nanotubes were calculated, and it is predicted that they depend on the structure of the rolling of a graphite sheet, and that such nanotubes should have metallic, semiconducting and insulating electrical characteristics [89]. However, even with these theoretical predictions, it is still very difficult to synthesize a specifically designed carbon nanotube in a very controlled manner, although several experimental efforts have been conducted [98]. In addition, several three-terminal nanotube structures have been proposed [99], which might meet the requirements of the necessary characteristics of information processing devices. A clever device design using carbon nanotubes would permit high-performance devices for future information processing. In the mean time, the first practical application of carbon nanotube in the electronics products environment would be field emitters for cathode
ray tubes and field emission displays [100], [101] because of their very high stability against an ambient atmosphere, and quite controlled growth capability at a designated location. Application to a probe tip of scanning probe microscope [102] is another quite promising potential of nanotubes.

E. Optical Devices

1) Light Detection Devices: As described in Section IV-B, the first single molecule light detection device was experimentally demonstrated by Fujihira in 1976 [38], [39]. Nature has also produced a “single molecule” light detection device, chlorophyll, in which electronic excited states generated by light in the molecules of a plant cell are transferred to the adenosine triphosphate (ATP) synthesis reaction site by hopping conduction [73]. The row of isolated molecules might not exhibit high-efficiency energy transmission in an artificial system because of the very high resistance. However, nature successfully transfers electrons at a very high quantum efficiency, almost unity, by precisely and cleverly designing the energy states of these molecules. An artificial system might be able to use a better strategy and maintain high-energy efficiency [103], if it is possible to exclude the unwanted resistance between the molecules. By using such a scheme, a very high-efficiency energy conversion system could be constructed using single molecule device systems. Molecules with very high cross-sectional area to light, preferably better than the one nature utilizes [73], would also be necessary to meet this objective.

2) Light Emitting Devices: Light emission from single molecules was detected by scanning near-field optical microscope (SNOM) [104] to observe the photoluminescence (PL) of a very dilute light-emitting molecule adsorbed on a substrate [105]. Though PL from a single molecule was successfully observed using the dilution method, single molecule electroluminescence (EL) has not been demonstrated yet. Organic EL devices are close to becoming practical these days by the striving efforts of scientists and engineers [106]–[108]; however, they are classified as thin film devices rather than single molecule devices. The electronic conduction, light emission and hole conduction layers are formed by layer-by-layer growth methods, and carriers pass through the molecular layers by the hopping conduction mechanism, in which the barriers between molecules prevent good carrier conduction and limit the quantum yield of the light emission to less than a few percent. Still, commercial products are already in the market, which suggests a good potential of organic EL display devices.

If single molecule light emitter devices, schematically shown in Fig. 17, are made practical, very effective light emission characteristics would be expected. The quantum efficiency would be almost unity, because the carrier injection efficiency, carrier transport efficiency and carrier recombination efficiency should be almost unity in this configuration, since there would be no carrier path other than that of the light emitting molecule itself. Of course, carrier recombination through phonon process might be inevitable in some cases, making clever molecular design necessary. The wavelength can be controlled by choosing appropriate molecular LUMO–HOMO structures at the carrier recombination site, so that an almost arbitrary wavelength light could be emitted from the single molecule system. In addition, the molecular system is extremely

Fig. 17 Schematic figure of the “single molecule light emitter device.” The molecules consist of an electron transport layer, light-emitting layer, and hole transport layer, and attached between two electrodes through, for example, thiol and carbonic reagent “connectors,” so that cathode–anode alignment can be ascertained, when they are fabricated by self-assembly technique.
Fig. 18 Schematic figure of single molecule-based data storage device using SPM technology: (a) “write” pulse application, (b) “erase” mode, and (c) “write” mode. An example of stored bits at a density of about $4 \times 10^{-6} \mu m^2$/bit (100 Tb/in$^2$) in a molecular system measured by STM.

flexible, and it can be used in any application, such as portable flexible paper-like displays, wall lighting systems and even outdoor sign boards. The reliability should be high enough for most of the applications, because there are very few, if any, unnecessary barriers between the electrode and the molecule, and heat and hot carrier generation would be avoided by the presumably very low operation voltages and very low power consumption. Thus, very high efficiency, low threshold, and low power laser operation should also be possible with the appropriate device design.

F. Information Storage Devices

Single molecule-based data storage devices could rely on any of several principles, such as charge retention, mechanical deformation, chemical conversion, chemical reaction, and refractive index change [109], [110]. The common principle is to put information in the molecule by supplying a charge, energy, or force from the scanning probe microscope (SPM) tip to the recording molecule. Fig. 18 shows an example of such a system, in which the electrical charges supplied from the SPM tip are stored on the self-assembled monolayer (SAM) of polyfluorocarbon molecules [111]. The charge, or the information, would have a retention time of more than several years. One bit of information requires less than 10 nm square, in fact, only one molecule of storage area is necessary for an ultimate storage device. Thus, the recording density would be as high as several Tb/in$^2$ ($6 \times 10^{-4} \mu m^2$/bit), even Pb/in$^2$ ($6 \times 10^{-7} \mu m^2$/bit), which is more than four orders of magnitude denser than the present systems. In this scheme, a STM tip induced chemical reaction [112], [113] mechanism would also be applied, which will make very stable data storage possible, although this scheme only makes “write once operation” possible.
Since most of the write/read operation would be performed by the scanning probe method [114], [115], the data rate would never be high enough for practical applications. Single SPM probes, including atomic force microscope (AFM) and SNOM can reach an intrinsic read/write operation frequency of as high as several megahertz. However, the data rate of present storage systems such as magnetic disks are already reaching 100 MHz, and a data rate of several times this will likely be achieved within several years. Therefore, a gigahertz level data rate will be needed for the systems being put in actual use in ten years time, which is not possible using conventional probe technologies. Multiple probe technology using micromachine technology [116] would make it possible to accelerate the data rate if there are thousands of parallel read/write tips. If 10^4 probes are integrated to form a read/write head, the individual tips should need only 100 kHz response to achieve a 1-GHz data rate, which is already within the achievable regime. Fig. 19 shows the schematic figure of the complete high-density data storage system with thousands of read/write heads operating in parallel on the same recording medium. A preliminary system based on this concept has already been partly demonstrated [117].

G. Single Molecule Detection Sensor Devices

Sensors work quite differently from above-described devices, since the principle of detection requires the molecular structure or electronic states to be affected by the detected substances. Some of the sensors use a field-effect scheme [118], in which numerous adsorbed molecules on the gate induce a potential change in the channel region. Another sensing principle, the quartz balance scheme, detects the change in the vibration frequency of the quartz beam when molecules adsorb on it [119]. Single molecule sensor devices would be able to detect a single molecule, exactly as in the detection systems of biosystems. For example, a single electron transistor principle can be applied, in which the very selective regand and receptor reaction takes place, submitting signals to the quantum dot by changing the gate potential of a single electron transistor, as schematically shown in Fig. 20. A very sensitive and selective single molecule detection sensor would thus be made possible.

H. Mechanical Devices

The mechanical motion within molecules has been seen as promising by several scientists, and several artificial “molecular machines” have been proposed [120]. However, can the force generated by the motion of a single molecule be extracted from such a tiny system and used to move an artificial outside object? Doing so would require overcoming the friction and viscosity around the molecule. Therefore, though the principle could be interesting and mechanical motion might also be attractive, the individual motion of the molecules would be undetectable, and those proposed systems would have very little impact on the real world.
VI. POSSIBLE MILESTONES TOWARD “SINGLE MOLECULE ELECTRONICS”

The ultimate goal of single molecule information processing devices is the “molecular super chip.” The core of the processor chip is made up of a 1-THz molecular processor and gigabyte cache memory, which are squeezed in about 200 \( \mu \text{m} \) square of area, due to the signal propagation limitation for 1-THz operation, while the periphery of the chip is occupied by several 10-GB semiconductor main memory mediated by interface circuits, in addition to the driver circuits of the peripheral devices such as the display and file memories. The total chip size would measure several centimeters square. Thus, the advantages of the very high-speed processing of single molecule devices are fully realized, while the man/machine interface is controlled by the peripheral semiconductor circuits. The “molecular super chip” would be used in a molecular personal supercomputer, schematically depicted in Fig. 21. In addition to the “molecular super chip,” the system has a terabyte molecular storage, a single molecule light emitting display, and a single molecule light interconnect for the highest possible performance. Of course, other functions, such as single molecular sensing devices to identify the user, can be integrated into the system. However, this destination cannot be reached in one step, and the following four milestones might have to be considered.

1) Measure the two-terminal conductance of a single molecule to verify the basic possibility of single molecule electronics devices.
2) Demonstrate the functions of two-terminal molecules, such as light emission to prove the functionality of single molecule devices.
3) Verify the operation of three-terminal molecules, such as transistor operation.
4) Integrate the functions of the “molecular super chip.”

For all of the single molecule device proposals described above, not even the electrical characterization of a single molecule has been thoroughly demonstrated yet, though several access methods to a single molecule have been proposed, and many “easy to measure” molecules have been synthesized. The next section will describe the current technology developments toward the first milestone for the realization of single molecule devices, and Section VIII will discuss the remaining three milestones.

VII. CHALLENGES FOR REALIZING SINGLE MOLECULE DEVICES: THE FIRST MILESTONE

The first milestone is to demonstrate the possibility to address a single molecule between two electrodes and to measure the electrical characteristics. This section summarizes the current status of the essential technologies needed to bring the ideas to reality, including theoretical prediction of the carrier transport through a single molecule, synthesis of appropriate molecules and development of conductance measurement technologies.

A. Prediction of Carrier Transport through Single Molecule

1) Theoretical Prediction of Electron Transmission through an Insulating Molecule: Generally, the length \( L \) dependence of electronic conductance \( G \) in an insulating molecule is expressed by a log-linear relationship, in which the slope becomes steeper as the bandgap \( E_g \) of the molecule increases

\[
G = G_0 \exp(-\alpha LE_g)
\]  

where \( G_0 \) and \( \alpha \) are material constants. Using (4), the conductance of molecules can be calculated and typical results are shown in Fig. 22 [121]. They clearly predict that the conductance or transmission of these molecules decreases monotonically with length in a logarithmic fashion, and that it reaches as low as \( 10^{-10} \) to \( 10^{-16} \) with a molecule length.
ductance differences, among the bridging atoms of oxygen, molecular system has been reported [124], in which the con-

much. The bridging atom dependence of conductance of a metals, since the Fermi levels of the two systems differ very 

tures of the molecules should be affected by connecting them 

tical measurements and applications. The electronic struc-

trode effects into account, which would be essential for prac-

be able to take place, so that the use of this guiding principle 

not to be used in the information processing devices. 

It is also predicted that if the carriers are injected by a res-

onant injection scheme [123], the conductance of even an insulating molecule would become very high, as shown in 

Fig. 23. However, the injection would have to be made pre-
cisely at the resonant level and a “logic swing” might not 

be able to take place, so that the use of this guiding principle 

might be very limited. Despite these limitations, the resonant 

injection scheme should be a very interesting subject, both 

theoretically and experimentally.

The above theoretical predictions do not take the elec-

trode effects into account, which would be essential for prac-
tical measurements and applications. The electronic struc-
tures of the molecules should be affected by connecting them 

through bridging atoms to the electrodes, which are usually metals, since the Fermi levels of the two systems differ very 
much. The bridging atom dependence of conductance of a molecular system has been reported [124], in which the conductance differences, among the bridging atoms of oxygen, sulfur, and selenium attached to xylyl derivatives, were sim-

ulated, and it was found that selenium would give the lowest resistance. It would be a very interesting challenge to experimentally verify this conduction phenomena in a single molecule. In addition, the electrode effect on the characteristics, including conductance, of a molecule has to be precisely evaluated, which still poses a high hurdle from the present hardware/software resources point of view.

2) Possible Quantum Transport and Permanent Ring Current through a Molecule: First principles predictions were reported on the electronic structures and current transport characteristics of electrode-molecule complex systems [125], [126]. Symmetrical and asymmetrical molecular systems were connected to bulk electrodes, and the transmission characteristics were examined. The results are depicted in Fig. 24, in which both the symmetrical and asymmetrical molecules exhibit very interesting phenomena. The electrons injected into the symmetrical system from the source electrode were found to have possible ballistic transmission characteristics of electrons through the molecule. Therefore, attaching a third electrode to one of the current paths would change the phase of the electrons passing through that side, making it possible to observe the phase interference of the electrons within a molecule. This theoretical prediction indicates a possibility of applying a single molecule system to a quantum computing architecture, which was described in Section II. In the asymmetrical system, a large permanent ring current flow within the molecule was predicted, which implies that a molecular magnet could possibly be made with smallest possible dimensions. Thus, logic and memory devices can be formulated using this magnetic characteristic of a single molecule system.

B. Necessary Characteristics of Molecules for Reliable Measurements for First Milestone

The next step toward the demonstration of the conduction measurement of a single molecule for the first mile-

stone is to synthesize appropriate molecules. The theoretical predictions described in Section VII-A1 imply that very low-resistance molecules have to be synthesized to achieve reliable measurements. The molecules listed in Section V-A could be the most probable candidates for the measurements so long as they fulfill the following characteristics. Appropriate “easy to measure” molecules would have the following characteristics:

1) solid and straight to connect the electrodes directly;
2) low resistance conductivity for reliable measurements;
3) “alligator clips” on both ends of the molecule for connecting to the electrodes;
4) relatively bulky insulating structures covering the conduction region for isolating the molecule from other molecules which can be called “molecular enamel wire,” and which also isolates the molecule from the substrate to avoid possible crosstalk.

Thus, the “easy to measure” molecule would have “alligator clips” attached to the two electrodes at both ends of the mol-

cule and a conducting body isolated from the substrate by
insulating “legs.” The most important part in the wire is, of course, the conducting part, which should have metallic characteristics or carriers supplied from dopants for very low resistance. In addition, the “molecular enamel wire” concept should simplify the wiring system in the future “molecular super chip,” because it would prevent any possible shorts between the wiring, and can easily construct multilevel wiring structures.

So many ideas of molecules for single molecule electronics have been reported, as discussed in Section V-A. However, two important subjects have to be considered before choosing the appropriate molecules:

1) electronic properties of a molecule will change if connected to electrode, such as metals and even to other molecules as pointed out in Section VII-A2, and theoretical prediction is indispensable for an appropriate molecular design;

2) LUMO–HOMO gap is usually large to give molecules insulating nature as described in Section V-A, and “zero bandgap” molecules have to be considered.

Thus, a choice of an appropriate molecule, combined with the technologies described in the following section, would make it possible to reach the first milestone.

**C. Two-Terminal Conductance Measurement Technologies**

In addition to the measurable molecules, the first milestone also requires us to develop conductance measurement technologies. This section summarizes the current status of the technology development for two-terminal conductance measurement of a single molecule: vertical and horizontal solid electrodes, piezo, and micromachine adjustable electrodes.

1) **Solid Electrodes:**

   a) **Placing molecules between two vertically stacked electrodes:** The simplest method to demonstrate the resistance of a single molecule is to sandwich the molecule between two vertically stacked bulk electrodes. A method was reported on the measurement of Langmuir–Blodgett (LB) multilayers, in which molecules with rectifying characteristics were sandwiched between two bulk electrodes, and their $I$–$V$ characteristics were demonstrated [127]. Similar results were also reported in which a thin-film multilayered structure was successfully fabricated to sandwich an LB film [128]. A demonstration was also made using mercury electrodes to sandwich alkanethiolate molecules and to measure $I$–$V$ characteristics [129]. The results indicate an exponen-
tial decay in conductance as theoretically predicted in the
Section VII-A1. Although these results do not clearly indi-
cate the single molecule characteristics, they do suggest that
the single molecule device concept is feasible. A recent ex-
periment also demonstrated that a monolayer of rotaxane was
formed between two aluminum electrodes, and $I-V$ charac-
teristics were measured [130]. Irreversible “switching” char-
acteristics were observed when oxidizing voltages were ap-
plied to the rotaxane molecules. However, the detailed mech-
anism remains to be clarified. In addition, this method would
not enable characterization of a single molecule, and further
contrivance might be necessary to confirm a molecule’s func-

**b) Use of solid nanoelectrodes to address a single
molecule:** Another method for measuring the conductance
of a linear molecule is to place a molecule between two
solid electrodes separated by a few nanometers [131]–[133].
Linear molecules are attached to the electrode structures
by either immersion in a solution or vacuum evaporation.
Considering the current status of nanolithography [52]–[54],
these achievements in fabricating few nanometer gaps are
quite notable. A typical AFM image is shown in Fig. 25
[134]. The shortcomings of this method are, of course:
1) the possibility of attaching too many molecules be-
   tween the electrodes;
2) leakage current through the surface of the substrate.
The experimental demonstration reported in [95] overcomes
these problems and provides very reliable results because it
was conducted in ultrahigh vacuum conditions. However, as
will be discussed in the later section, the molecular super
chip, which is the core of the “single molecule personal super-
computer,” would have to be fabricated on a substrate, and
this single molecule connection approach should play a very
important role for realizing the future molecular information
processing system.

2) **Adjustable Electrodes:**

**c) Nanconnection technology using piezoelectric de-
vices:** Another possible method for measuring single mole-
cule conductance is to use piezoelectrically driven devices.
Two methods have been reported so far: one is called “me-
chanically controlled breakable junction (MCB)” [135], and
the other uses STM [136]. The former pushes very thin gold
electrodes attached with molecules by piezoelectric devices
to widen the gap between the electrodes, enabling the gap-
width to be controlled down to the picometer ($10^{-12}$ m)
regime. The latter uses STM to image surfaces, on which a
monolayer of molecules is arranged, and the STM tip serves
as the upper electrode to attach to the molecule from the top.
If only one size of molecule is arranged in the monolayer,
[127], there is a good possibility for the STM tip to attach to
several molecules at the same time, while if the target mol-
ecule is sticking out from the surface, by inserting longer
molecules among the shorter ones, then the longer molecules
prorate from the other molecules [136], and a single mole-
cule can be accessed by the STM tip. All the reported ex-
periments found that the resistance of a single molecule can
be of the order of several megohms. The reason for the very
high resistance might be due to the insulating nature of the
measured molecules, and at the same time, the high contact
resistance between the STM tip electrode and the molecule.
The possible problem of this measurement method is that the
tip apex has not been investigated, and there still remains a
possibility that the electrodes may be relatively flat, and may
accidentally have many connecting molecules between them.

Another possible nanconnection formation technology is
called needle formation and tip imaging (NFTI). A needle
structure as small as 1.5 nm in diameter and up to 10 nm in
height have been grown on a silicon surface [137], [138], as
shown in Fig. 26. This should be small enough to address a
single molecule on the top. The nanoneedle might be made
up of silicon atoms, and substances that selectively react with
silicon, such as carbonic acid, would form chemical connec-
tions to the apex of each nanoneedle quite controllably and
selectively. The remaining problem is to make the structures
strong enough to stand against the high electric field and the
mechanical force. The nanoneedle also permits precise char-
acterization of the STM tip apex structures [137]. A carbon
nanotube might also be used for addressing single molecule,
because of its very small diameter and mechanical strength [139].

d) Micromachine technology for addressing a single molecule: Micromachine technology [140] was developed to fabricate a miniature STM for single molecule addressing [141]. A scanning electron microscope (SEM) micrograph of the micromachine STM is shown in Fig. 27(a). The comb electrodes move the main body back and forth by applying voltages between them and generating electrostatic force. In order to investigate whether the area between tip and sample is small enough to accommodate a single molecule, the vacuum tunneling gap was investigated using transmission electron microscopy (TEM). The results indicate that the area between the two adjacent electrodes is so small that a single molecule could connect the two electrodes, as is also shown in Fig. 27(b) [142]. The results also suggest that a single molecule might be observable by TEM if addressed between the two electrodes, which would permit quite clear evidence for measuring the characteristics of a single molecule.

VIII. TOWARD THE GOAL: NEXT THREE MILESTONES

A. Functions of Single Molecule—The Second Milestone

The second milestone is to demonstrate the functions of the molecules by using the two-terminal measurement technologies described above. The major functions of two-terminal single molecule devices would be rectification, light emission, sensing, and ballistic transport of carriers. The appropriate molecular design should take the electrode as well as $I-V$ injection effects into account, by which not only the molecular structure itself might be changed, but the characteristics could also be affected. Therefore, theoretical prediction of the electronic structure of a single molecule should be very important from the design/fabrication point of view. Thus, the first single molecule device would be made practical, which is essential for the further development of single molecule electronics for advanced information technologies.

B. Three Terminal Connection Ideas—The Third Milestone

The third milestone toward single molecule electronics is to connect the three terminals to the molecules. The selective reaction between a specific part in a molecule and the corresponding atom species on a substrate can make this scheme possible [143]. For example, a selective reaction takes place between a sulfur atom within a molecule and a gold atom on a substrate as well as carbonic acid and a silicon atom. Another possible candidate is to use an anchoring molecule [144], which stands by itself on the substrate with its three legs. Thus, by choosing appropriate reagents, molecules can be placed at the designated positions on the surface of the substrate. Fig. 28 indicates schematically how the selective reaction between gold and thiol, and between silicon and carbonic acid, would make it possible to place a three-terminal molecular device at a designated place very precisely. Thus, a circuit, like the one depicted in Fig. 28, would be constructed in a “self-assembled” manner. In this scheme, a theoretical characterization should also be very important to predict the performance of the very large molecular system, and therefore, further progress in simulation technologies is indispensable.

C. Integration of Single Molecule Devices on a Chip—The Final Milestone

As described above, the final destination of the single molecule electronics concept is to build an information processing system, with a T-FLOPS molecular processor, a terabyte molecular file system, high efficiency single molecule display and single molecule light interconnect, as schematically shown in Fig. 21. The fabrication processes should be much less complicated as compared with those of CMOS ICs shown in Table 3: i.e., substrate preparation, molecule assembly, and final packaging. Thus, the cost would be much less than the conventional semiconductor device, including clean room cost.

An idea has been proposed in which the single molecule circuits are connected to the semiconductor circuits [145]. It is very possible that signal amplification circuits
also have to be inserted between the core molecular circuits and the peripheral semiconductor circuits due to possible differences of the signal levels between the two circuits. The peripheral devices, such as displays and storage devices might have to be driven by conventional semiconductor devices, because the signal levels of molecular devices would be quite different from those of the peripheral devices, though the signals might be able to transmit directly among those devices.

D. Toward the Goal: Conquering Technological Difficulties

As has been discussed previously, those milestones are not easy to accomplish. Several critical issues were described in the sections: 1) resistance of a molecule (Sections V-A1 and VII-A); 2) contacting individual molecules (Sections VII-B and C); 3) molecule–molecule interconnect (Section VIII-B); 4) meeting the criteria of information processing devices (Section III-D); and 5) assembly of molecular computer (Section VIII-C). Item 5) might also be solved by an advancement in molecular synthesizes, i.e., a 1-kb \((32 \times 32 \text{ bit}^2)\) molecular “memory mat” based on the memory cell described in Fig. 8(a), and a 100-gate logic assembly based on the gates shown in Fig. 8(c) might be synthesized for production environment. The “memory mats” would formulate a gigabit “memory block” by arranging them by \(1000 \times 1000\). They can be assembled on a substrate also by selective reaction described in Section VIII-B. Accurate theoretical prediction of the performances of the “memory mats” and “logic assembly” would be indispensable for the design and production of molecular supercomputer described in Sections VI and VIII-C. An intimate multidisciplinary research among molecular synthesis, materials science, device physics, theoretical design and information science would definitely be required to achieve the final goal for high performance single molecule information processing technologies.

IX. CONCLUSION

This paper discussed the prospects for single molecule devices, including switching devices, light-emitting devices, storage devices, and sensing devices for future information processing and other advanced applications. The operation principles are based on the characteristics of a single molecule, such as single electron transfer, direct electron–hole recombination, magnetic/charge recording, and regand–receptor reaction. A possible architecture is also considered, which is suitable for molecular information processing systems. A personal supercomputer which would operate at about three orders of magnitude higher performance, and permit single machine P-FLOPS computational power, would be made possible by the “molecular super chip,” together with very high-density single molecule storage systems and high efficiency single molecule display devices. Four milestones were proposed toward the final destination, and current status of the technology development was reported, including theoretical considerations, molecular synthesis and measuring apparatus development. An intimate multidisciplinary study among molecular synthesis, materials science, device physics, theoretical design, and information science, would definitely be required to achieve the final goal for high-performance single molecule information processing technologies.

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References


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