

Organic-Inorganic Hybrid Devices (Single-Molecule Technology)

Takahiro KAJI, Toshifumi TERUI, Toshiki YAMADA, Rieko UEDA, Shin-ichiro INOUE, and Akira OTOMO

We developed organic-inorganic hybrid photonic and electronic devices by combining single molecules with inorganic mediums or nanoelectrode gaps. We demonstrated that our novel photonic devices combining single molecules and photonic crystals can improve the efficiency of light use of molecules and control the photofunctions of the molecules. We investigated properties of a single-molecule single-electron transistor (SET) in which a nanoelectrode gap was bridged by a π -conjugated molecule, and a nanoparticle SET in which gold nanoparticles were coupled through multiple molecular junctions.

1 Introduction

In recent years, organic materials have been regaining their popularity as materials that are equal to or better than inorganic materials in their functionality, or are able to complement or mutually complement inorganic materials, and the incidence of their actual use in optical and electronic devices is spreading. Not only the development of organic materials themselves, but the technological development to integrate them into inorganic devices is contributing massively to their practical application and industrialization. Furthermore, it will become important in the development of optical and electronic devices to use organic materials scaled down from bulk sizes to nanometer sizes and even molecular sizes. Scaling down organic materials to molecular sizes will enable the manipulation and control of single photons and electrons, which is difficult to do with bulk materials. This is expected to lead to the development of ultra energy efficient optical and electronic devices, and devices capable of information processing based on quantum principles. Even in such devices that use organic materials on molecular scales, it will be important to also use inorganic materials in hybrid devices to make efficient use of their quantum functions, or for inputting and outputting signals. This paper will give an outline of the results of research our group has been carrying out in the development of organic-inorganic hybrid (1) photonic devices and (2) electronic devices that combine inorganic media and nanogap electrodes, made by using singular molecular systems and top-down technolo-

gies such as fine processing technology. In regard to (1) photonic devices, we demonstrated that highly efficient generation of single photons is possible, and that it is possible to control the optical functions of molecules by controlling their emission or the lifetime of the electronically excited state through the use of single molecule systems combined with inorganic media. Furthermore, in regard to (2) electronic devices, we demonstrated that it is possible to build nano-electrode connections making use of the diversity of organic materials, and that single electron transistor control is possible too, making use of functional molecules.

2 The Organic-inorganic hybrid photonic device (Single molecule technology 1)

2.1 Introduction

2.1.1 The single-organic-molecule-inorganic hybrid photonic device

Optically functional organic materials are attracting attention for their uses in organic EL, photoelectric conversion devices, optical switching devices, laser devices, etc. Such photonic devices that use bulk organic materials were used mainly as traditional means of generating, converting and manipulating light. On the other hand, the single organic molecule, which is a form of organic material that has been microminiaturized to the extreme, can be used as a single quantum system. For this reason high expectations are held for the single molecule, like the single atom or the quantum dot, for its use in devices^{[1][2]}

for generating and receiving single photons, necessary for quantum information communication and quantum cryptography, as well as for use in optical switching and laser devices. The advantages of using single molecules are that there are a wide variety of molecules providing a range of functions depending on the molecular design, they can be used within solids allowing easy handling, and there are no differences between molecules allowing use of photons whose wavelengths have been accurately tuned by placing them in appropriate environments.

In order to create photonic devices using single organic molecules, simply scaling down the size of organic materials to nano or molecular levels does not allow sufficient interaction with the light, making it difficult to attain practical functions. Making use of single molecules as molecular devices requires development of technology for efficient interaction between light and the single molecules with extremely small absorption cross sections, efficient extraction of light from the single molecules, and gaining free control over the optical functions of the single molecules. We therefore focused our attention on photonic crystals (PC) that allow optical confinement and control of light propagation in nano scale spaces. Using non-light absorbing dielectric substances as the material for photonic crystals prevents loss of light due to absorption, making it suitable for use in single molecule photonic devices that use faint light. In the first half of this paper, we will report on the results of research carried out by our group into creating a new organic-inorganic hybrid photonic device combining a photonic crystal with a single molecule system (Fig. 1).

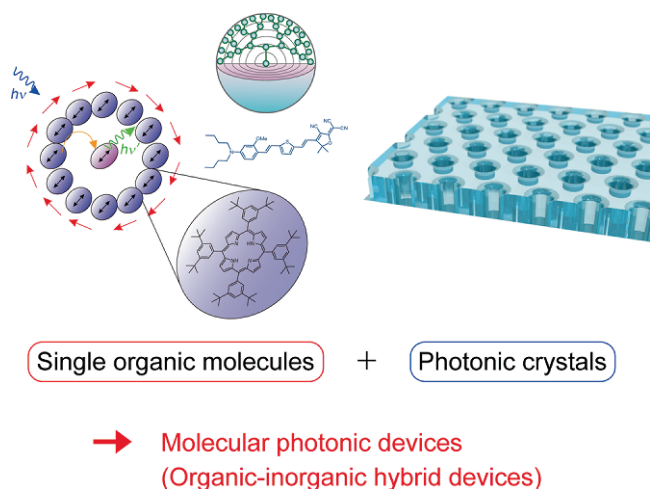


Fig. 1 Conceptual diagram of the single-organic-molecule-inorganic hybrid photonic device

2.1.2 Using single molecule spectroscopy and photonic crystals

The detection of optical signals from single molecules dates back to 1989 when absorption signals from single molecules were detected^[3], and fluorescence excitation signals from single molecules were detected^[4] the following year. Then the generation of on-demand single photons at room temperature using single molecules was demonstrated^[1] in 2000. Since 2000, high sensitivity optical detectors such as avalanche photo diodes and photomultiplier tubes came to be used widely, leading to advances in spectroscopic research into single molecule systems with a variety of optical functions such as light-harvesting^[5] and optical switching^[6]. However, much of the single molecule spectroscopic research so far had aimed to clarify the properties of the molecules themselves, and there had been little research focusing on their application in devices. For this reason, not much research and development had been carried out into single molecule photonic devices that made use of nano structures consisting of metals and inorganic materials enabling the control of light on nanometer scales. In particular, research had been carried out into observing the fluorescence enhancement of single molecules in plasmonic devices using metallic nano structures^[7], but little research had been carried out with the aim of boosting the efficiency of light utilization and controlling the optical functions of single molecules with photonic devices (photonic crystals) making use of the periodic structure of dielectric substances. Under such circumstances, we began our research by searching for new photonic crystal materials that could be combined with single molecule fluorescence spectroscopy^[8], and succeeded in boosting the efficiency of optical excitation and light extraction of single molecules through the use of photonic crystals^[9]. We also succeeded in pioneering the control of emission from single molecules making use of the photonic band gap effect^[10]. These research results are vital in the fundamental technology to control light utilization and the optical functions of single molecule systems using nanophotonic structures, and we have great expectations for our results to promote the massive expansion of research in this area.

2.2 Developing a photonic crystal platform to control light emission from single molecules

2.2.1 Creating a low background light emitting photonic crystal

Semiconductors and inorganic materials such as Si,

InP, GaAs, etc., are examples of photonic crystal materials that have so far been used. These materials have been used in a lot of research because of their large refractive indexes and the fact that they allow generic micromachining. An important property required of photonic crystal materials needed to control the light emission of minute quantities of organic materials such as single molecules is that the background light emission of the photonic crystal itself be extremely low so as not to drown out the faint fluorescence signal from the organic material. Furthermore, spectroscopic research into single molecules has advanced through the use of avalanche photo diodes and photo multipliers that allow detection of light with high quantum efficiency within the visible light range. Another requirement is that they can be used as photonic crystal material (they must be transparent) within the visible light range. As materials that fulfill these criteria, we decided to use inorganic oxide materials such as tantalum pentoxide (Ta_2O_5) and titanium dioxide (TiO_2). The refractive index of tantalum pentoxide is around 2, and it is transparent within the ultraviolet and visible light range of around 300 nm and over. Furthermore, the refractive index of titanium dioxide is around 2.4, but its use is limited to the wavelength range of around 400 nm and over. These oxide materials are known to emit light from their oxygen-deficient centers, becoming a cause of background light emission. We removed the oxygen-deficient centers by thermally annealing the substrate in an oxygen atmosphere, to succeed in reducing background light emissions^[8]. Figure 2(a) shows a schematic diagram of the two-dimensional photonic crystal substrate (slab-shaped) formed by e-beam deposition of tantalum pentoxide on a cover glass, which was then micromachined through e-beam lithography and dry etching. Furthermore, Fig. 2(b) shows the dependence of the strength of the excitation light on the background light emission of various substrates. In the experiment, we used

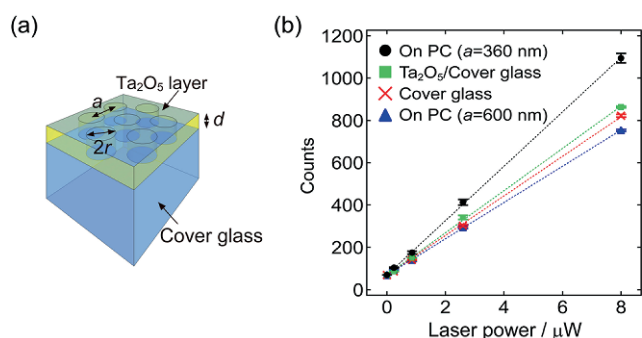


Fig. 2 (a): Schematic diagram of tantalum pentoxide photonic crystal (b): The dependence of the strength of the excitation light on the background light emission

a 100x objective lens with a numerical aperture of 0.90, and irradiated the substrate with the second harmonic beam (488 nm) of a picosecond Ti: sapphire laser to detect the emission of light with a photo multiplier. Regardless of the strength of the excitation light, the background emission of light by a tantalum pentoxide substrate was about the same as that by the cover glass on its own. In the photonic crystal with a lattice constant [spaces between the holes (a) arranged in an orderly fashion] of 360 nm, a slight increase in background light emission was seen. But even with the excitation light strength in general single molecule fluorescence measurements (2.6 μW), their background light emission was low, at around 410 counts/second. It was confirmed that the photonic crystal substrate we created could be used in single molecule fluorescence measurements.

2.2.2 Enhancing the fluorescence of single molecules using two dimensional photonic crystals

Next, we carried out experiments with the aim of observing the enhancement of fluorescence through the efficient optical excitation of single molecules, and by boosting the efficiency of light extraction by making use of the actual effects of photonic crystals^[9]. The resonant frequencies of the excitation light and the fluorescence change depending on the value of the photonic crystal lattice constant. So an enhancement in the fluorescence of the photonic crystal should be observed at a certain lattice constant value. Using polymethyl methacrylate (PMMA) as the matrix, a fluorescent pigment of a perylene bisimide derivative was spin-coated onto the photonic crystal substrate at ultralow concentrations. Figures 3(a-d) show the typical results of confocal fluorescence microscope

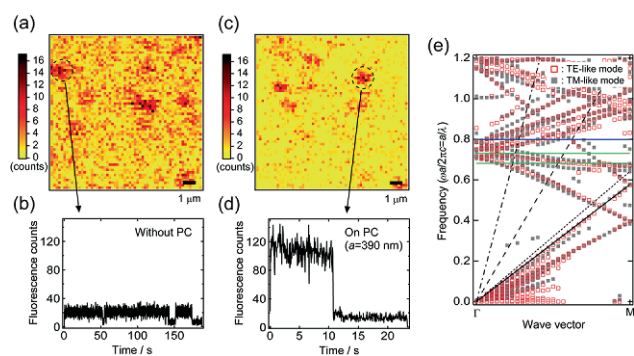


Fig. 3 (a, b): Area outside the photonic crystal (c, d): Within the photonic crystal area with a lattice constant of 390 nm (a, c): Confocal fluorescence microscope images (b, d): Changes over time in the fluorescence intensity of the single molecule (e): Photonic band structure

images (a, c) of the area outside the photonic crystal (a, b) and within the photonic crystal area with a lattice constant of 390 nm (c, d), and the corresponding changes over time (b, d) in the fluorescence intensity of the single molecule. The single-stage drop in the fluorescence intensity to a background level is in response to photobleaching of the single molecule. In the photonic crystal with a lattice constant of 390 nm, over three times the fluorescence enhancement was observed on average. An electromagnetic field simulation was carried out using the finite-difference time-domain method to examine the mechanism behind the enhancement of fluorescence, and the photonic band structure of the transverse electric (TE) field and transverse magnetic (TM) field modes were ascertained (Fig. 3(e)). The blue and green lines in the graph show the frequency of the excitation light and the fluorescence peak of the perylene bisimide derivative respectively, when the lattice constant is 390 nm. When an objective lens of high numerical aperture is used, the excitation light and fluorescence also have a wave vector component in the horizontal direction along the substrate, so the coupling between the light and mode becomes an important factor across a wide area between Γ and M. The excitation light wavelength indicated by the blue line and many modes come together (particularly around the Γ point), and this is thought to indicate excitation light enhancement through resonance between the excitation light and the structure. The crossing over of the fluorescence peak wavelength indicated by the green line with many modes is thought to indicate the enhancement of the fluorescence extraction efficiency due to resonance between the fluorescence light and the structure. These two mechanisms can explain the enhancement of fluorescence.

2.2.3 Controlling single molecule light emission using “Nano Radiation Fields”

One of the properties of photonic crystals worthy of special mention is their ability to control the number of electromagnetic modes (electromagnetic local density of states) included in their unit volume and unit frequency. According to Fermi's golden rule, the radiation (light emitting) rate of an emitting dipole depends on the density of states of light in a spatial position where a dipole exists. In other words, if a “nano radiation field” could be created in which the density of states of light could be controlled freely through the use of photonic crystals, it would not only become possible to boost the efficiency of light utilization by the molecule, but it would also allow the

fluorescence emission rate of the molecule itself to be controlled, or the controlling of the electronically excited-state lifetime, which determines the reaction yield of various photochemical and photophysical processes. This will allow the controlling of optical functions of molecular photonic devices, or the creation of new functions such as laser oscillations. In the experiment described below, we used a photonic crystal with a photonic band gap (PBG), which is the wavelength range at which the density of states of light becomes zero (in reality it becomes extremely small), to control the fluorescence emission rate of a single molecule on a photonic crystal¹¹⁰. When the wavelength range of the emission spectrum of the molecule and the photonic band gap overlap, the light mode necessary for the molecule to emit light does not exist, leading to a massive reduction in the fluorescence emission rate (Fig. 4). This is expected to considerably extend the fluorescence lifetime.

Figure 5(a, b) shows a schematic diagram and SEM images of a photonic crystal with an air bridge structure made of titanium dioxide. The photonic crystal produced has a photonic band gap for the transverse electric (TE) field mode, which can be seen from its photonic band structure (Fig. 5(c)). As shown in Fig. 6, when the lattice constant is 240 nm, the overlap between the wavelength range of the fluorescence spectrum of the perylene bisimide derivative and photonic band gap becomes largest, and the light emitting rate is expected to drop dramatically. Measuring the fluorescence of a single molecule was carried out with a confocal fluorescence microscope shown in Fig. 6(c). Figure 7(a) is a fluorescence image of the air bridge region to which pigment has been applied. Numerous fluorescence spots were observed believed to correspond to the location of single molecules. Figure 7(b-g)

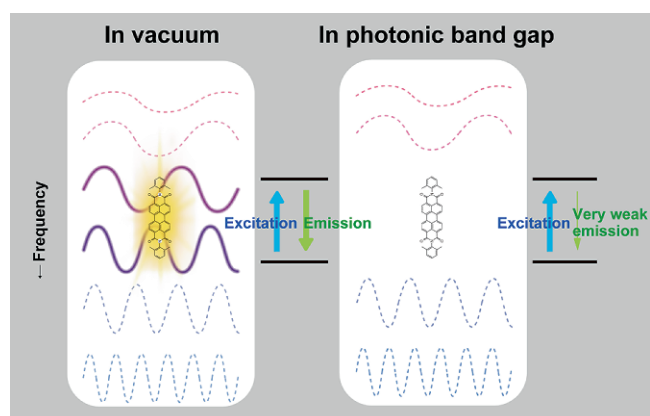


Fig. 4 Conceptual diagram of molecular light emission control by the photonic band gap

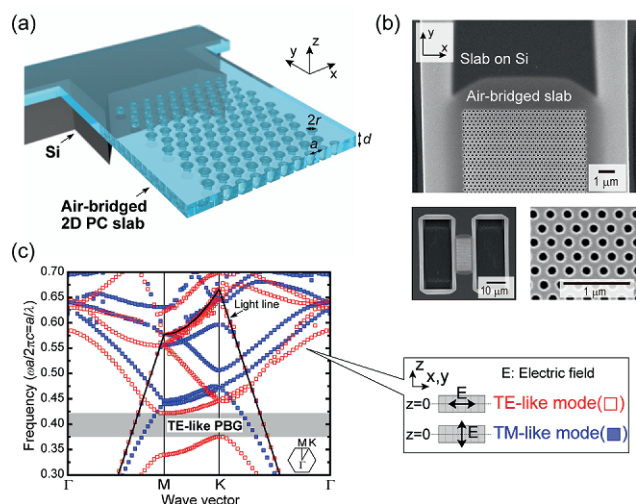


Fig. 5 (a): Schematic diagram of a photonic crystal with an air bridge structure (b): SEM images (c): Photonic band structure

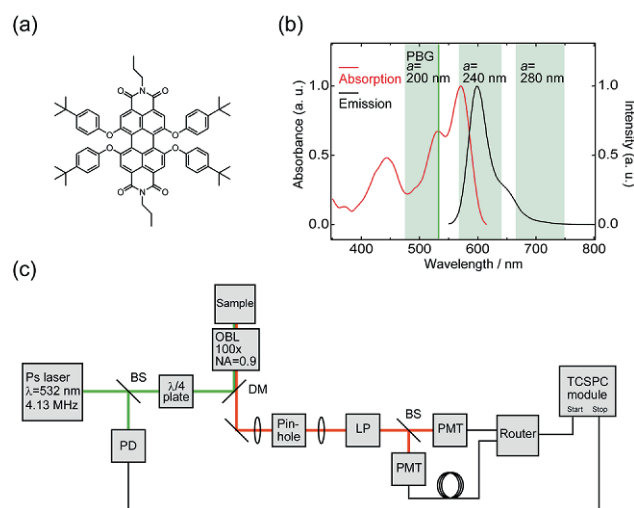


Fig. 6 (a): Structure of the light emitting pigment used in controlling light emission (b): Wavelength range of light emitting pigment absorption, fluorescence spectrum and photonic band gap (c) Schematic diagram of experimental setup

shows typical results in the changes over time in the fluorescence intensity (b, e), coincidence histograms (c, f), and fluorescence decay curves (d, g) of single molecules outside the photonic crystals (b-d) and on the photonic crystals (e-g) with a lattice constant of 240 nm. The lowered number of events at the $t=0$ of the coincidence histogram shows the emission of single photons from the single emitter, and this ensures the measurements of fluorescence of single molecules. Analyzing the fluorescence decay curve revealed that there were molecules in which the fluorescence lifetime was extended a maximum of 5.5 times (28.6 ns) on the photonic crystal, compared to the normal fluorescence lifetime of the perylene bisimide

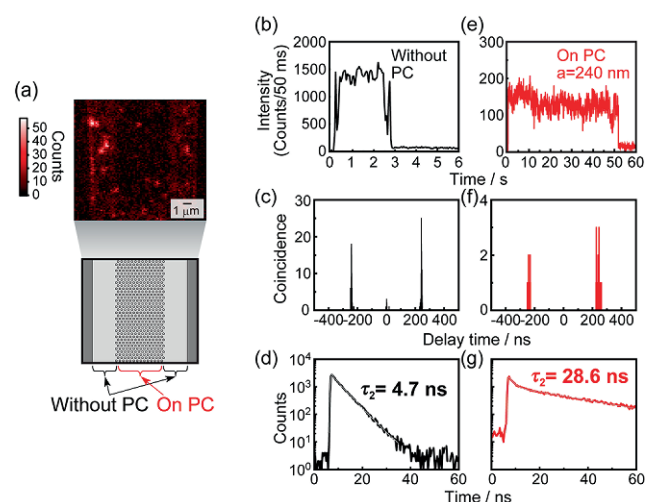


Fig. 7 (a): Confocal fluorescence microscope image of the air bridge part to which pigment has been applied (b-d): Area outside the photonic crystal (e-g): Photonic crystals with a lattice constant of 240 nm (b, e): Changes over time in the fluorescence intensity of single molecules (c, f): Coincidence histograms (d, g): Fluorescence decay curves

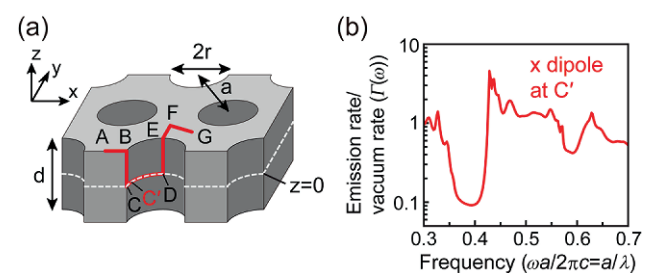


Fig. 8 (a): Location of emission dipoles (b): Results of the calculation of the fluorescence radiation rate of an x emission dipole at point C'

derivative ($\sim 5\ \text{ns}$).

To prove that this extension of the fluorescence lifetime is due to the effect of the photonic band gap, we calculated the fluorescence radiation rate of the emission dipoles set in various locations on the surface of the photonic crystal (Fig. 8(a)). Figure 8(b) shows the result of the calculation of the fluorescence radiation rate of a horizontal (in the direction of x) emission dipole set inside the hole at the plane of symmetry of the z axis (point C'). The fluorescence radiation rate was found to drop dramatically (~ 0.1 times) within the frequency range (0.36–0.42) corresponding to the photonic band gap. The maximum calculated ratio of extension of the fluorescence lifetime, taking the fluorescence quantum yield of the pigment (0.96) into account, was 5.9 times the normal lifetime, which agreed closely with experimental values. At the same time, it was found that there was no drastic drop in the fluorescence radiation rate when the emission dipole was

set vertically, and it became clearly apparent that the positioning of the molecules is a vital factor. The dramatic extension of the fluorescence lifetime observed in our research had rarely been observed up to now, even in bulk organic materials. This is because the alignment of emission dipoles in bulk organic materials is random and controlling their light emission would require three dimensional photonic crystals with three dimensional photonic band gaps in the visible light range, but the production of such photonic crystals is not easy even with current technology. In other words, we believe we were successful in observing the dramatic extension of fluorescence lifetime for the first time, thanks to our method of combining single molecule fluorescence measurements with two dimensional photonic crystals which have two dimensional photonic band gaps.

2.2.4 Prospects for the future of single molecule photonic devices

As for the prospects for the future of single molecule photonic devices, we plan to continue our research in aiming to create single molecule laser devices or optical switching devices, devices for manipulating single photons, etc., making use of the combination of microresonators with single molecules set on photonic crystals. We also hope to establish methods for building single-organic-molecule-inorganic hybrid photonic devices, through not only top-down methods of positioning molecules, but also bottom-up methods of self-organization and other manipulation technologies using probe microscopes such as STM and AFM to position molecules, or technology to control orientation, as well as the development of technology to overcome photodegradation of molecules.

3 Organic-inorganic hybrid electronic devices (Single molecule technology 2)

3.1 Introduction

The electronic device function of a “single-molecule junction,” in which a pair of electrodes is joined together by a single molecule, was first reported in 1974 by Aviram and Ratner^[11]. By creating a p-n junction in a single molecule, they demonstrated theoretically that rectification of the electrical conduction occurs in it. Later, Carter, et al. suggested its application in molecular integrated circuits to open up a new field in molecular electronics research^[12]. Numerous varieties of molecular devices such as memories and switches based on functions unique to molecules, and

components such as molecular wires to join the devices, have so far been proposed or synthesized^[13].

In terms of charge transfer within organic molecules, some molecules are superior to inorganic ones, as can be guessed from the outstanding qualities of π -electron materials such as graphene and carbon nanotubes. In addition, organic materials are generally considered to be fragile, but by removing water, oxygen and other reactive impurities, it is possible to give them ample durability for use in electronic devices.

Organic molecules are normally microscopic structures on nanometer size scales. They make excellent nanomaterials that allow uniform energy structures and the designing of unique properties based on them. This allows the diversification of device functions and freedom in production processes in single molecule electronics. Using organic materials as isolated molecules reveals a new aspect of electron materials. Great expectations are held for the roles that molecular materials will play in energy-saving and the next generation of highly functional electronics.

We have been engaging in research and development of single electron transistors (SET) that use single molecules as new, power-efficient devices. The SET is an ultra energy efficient device^[14] that controls the transfer of each and every electron by making use of the Coulomb blockade phenomenon, based on the charging energy of nanometer sized microelectrodes called Coulomb islands. It also has potential as a highly functional device allowing logical operation through improvisation of the device structure such as by giving it multi-dots or multi-gates^[15]. Based on the principles of the device however, it requires nanometer sized microstructures that are subject to the limitations of micromachining technology, so the high functionality of the SET has not yet been fully realized. We focused on the fact that organic molecules make excellent nanostructures, and we believed we could overcome micromachining limitations by making use of them in the SET to draw out the full potential of its high functionality. Two main types of SET using joined molecules have so far been reported. The first is a “single molecule SET” that uses the organic molecule itself as the Coulomb island^[16]. The second is the “nanoparticle SET” that uses the organic molecule as a tunnel layer to separate the Coulomb island, the source and drain electrodes made of metals, semiconductor particles, etc.^[17]. The latter is not a single molecule device in the true sense of the word, but it can be regarded as a system that utilizes the high-order functionality resulting from the joining of multiple molecules in series. In the latter half of

this paper we will report on the outline of research results in this area.

3.2 The single molecule SET

The SET consists of source, drain and gate electrodes and microelectrodes known as Coulomb islands. Electrical charges can be transferred between the Coulomb islands and source and drain electrodes through the tunnel layer, and they are separated from the gate electrodes by an insulating layer. When an electrical charge is transferred between the Coulomb islands and source and drain electrodes, the electrostatic energy of the Coulomb islands increases by just $e^2/2C$. Here e represents the elementary electric charge, and C is the capacitance of the Coulomb islands. When the size of the Coulomb islands is reduced to a nanometer scale, it creates a system in which the electrostatic energy is sufficiently greater than the thermal energy (normally at low temperatures below 10 K). When this happens, energy to compensate for the increase in electrostatic energy must be supplied from the power source, or the transfer of an electrical charge through the Coulomb island becomes impossible even if it is only a single electron. This phenomenon is known as the Coulomb blockade, and it is a fundamental principle on which the operation of the SET is based. The SET is a device that makes use of this phenomenon to change the potential of the Coulomb island, to control the charge transfer between the source and drain electrodes^{[14][15]}. The smaller the size of the Coulomb island, the bigger the electrostatic energy will be, and the Coulomb blockade will come into play, so a more practical SET can be built that operates at high temperatures. Molecules are around 1 nm in size, and the electrostatic energy of isolated molecules is over 1 V. Therefore, it is hoped that using molecules as Coulomb islands will allow the building of high performance SETs with unique functions that can be operated at room temperature^[18]. These are the advantages of the single molecule SET.

The single molecule SET consists of electrode pairs (nanogap electrodes) that face each other with gaps of less than a few nanometers between them, π -conjugated system molecules (Coulomb islands) that bridge the gap between electrodes, and gate electrodes (Fig. 9). We made nanogap electrodes through the electromigration (EM) method described in previous research carried out by Park, et al^[19]. In the EM method, fine Au leads etched by e-beam lithography are electrically disconnected to make nanogap electrodes, which in our design was 100 nm, 200 nm, and

20 nm in width, length and thickness respectively (Fig. 9(a, b)). The width of the gap obtained by this method is not uniform, normally ranging from a few to several tens of nanometers. But it has been reported that gap electrodes with extremely narrow gaps can be made and duplicated by controlling the feedback of breaking conditions^[20]. Molecules are joined by bridging the gap between nanogap electrodes with measured molecules, but a method of controlling the number of molecules and their orientation in bridging gaps between nanogap electrodes fixed onto the substrate has not yet been established. The most common method currently used to stochastically bridge the gap between gap electrodes is by dripping a molecule solution onto the surface of the electrodes and letting it dry, or using a gold-thiol reaction to attach molecules to the electrodes^{[16][19]}. Refer to a previous report for details of these processes^[21].

Figure 10 shows the SET properties observed in the porphyrin derivative molecule bridge we created. The gate voltage is shown along the horizontal axis (V_G), the drain voltage is shown along the vertical axis (V_D), and the color scale shows the differential conductance (dI/dV_D). The

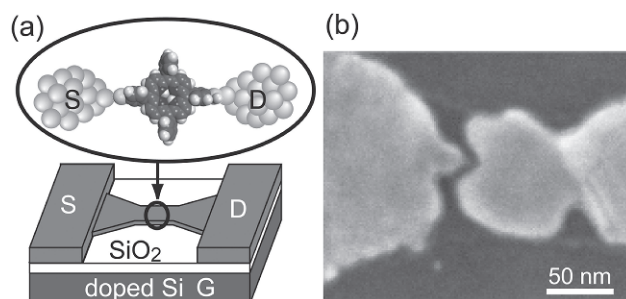


Fig. 9 (a): Schematic diagram of a single molecule connection (b): SEM image of nanogap electrode made by the EM method

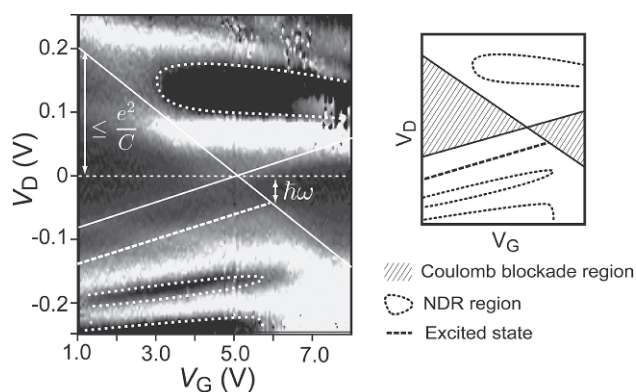


Fig. 10 The differential conductance and gate voltage mapping of the porphyrin SET

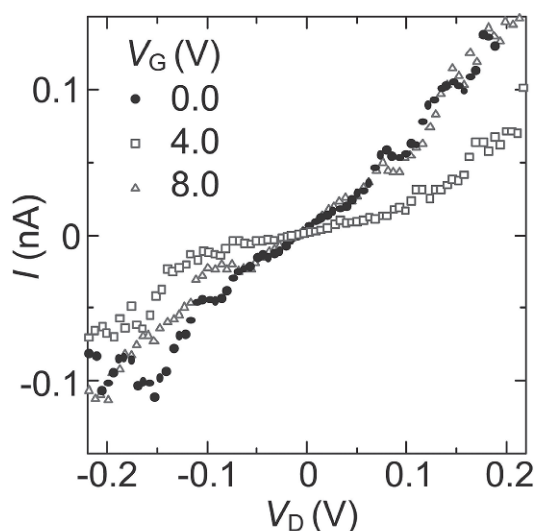


Fig. 11 Dependence on the gate voltage of porphyrin molecule current and drain voltage

geometric pattern seen in Fig. 10 is unique to the SET, and it is known as the Coulomb diamond. The charging energy of the Coulomb island (e^2/C) estimated from this characteristic is over 200 meV, and it is considerably big even when compared to the charging energy of the SET made through lithography^[22] or the nanoparticle SET, which will be mentioned later. This is thought to reflect the size of the charging energy of the molecule. However, in nanogap electrodes made through the EM method, metal microparticles are scattered about between the electrodes during formation of the nanogap. This then functions as the Coulomb island, and it has been reported that the SET characteristics are observed regardless of whether there are molecules or not^[23]. Therefore, observing just the SET characteristics is not sufficient to conclude that it comes from the molecules. One of the characteristics of the SET with Coulomb islands made of molecules is the presence of excited levels resulting from molecular vibration^[16]. The excited levels within the Coulomb islands are observed as straight lines running parallel to the sides of the triangle (ground state). Looking at Fig. 10, you can see the excited levels around the 40 meV area from the ground state. This coincides with the vibrational mode ($334\text{ cm}^{-1} \approx 41\text{ meV}$) of the porphyrin frame^[24]. Evidence of negative differential resistance can also be seen in Fig. 10. These results can be explained when we assume that the energy levels of the Coulomb islands are discrete^[25]. From these results it is believed that the porphyrin molecules are functioning as the Coulomb islands, and not the metal microparticles that were scattered about between the electrodes during the EM process, in this device.

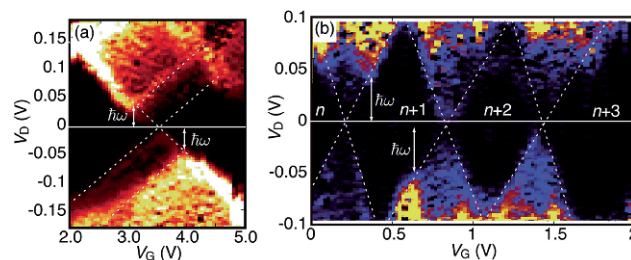


Fig. 12 (a): Dependence on the gate voltage of the differential conductance of the C60 SET and drain voltage (b): Oligothiophene nonamer SET

Figure 11 shows the current-voltage characteristics (I - V_D) of this device at room temperature. The Coulomb blockade is not clear, but you can see the I - V_D curve being modulated by the gate voltage. This change is not directly proportional to the gate voltage, but it shows periodicity in that it momentarily becomes depressed before increasing rapidly again, suggesting that single-electron transport prevails even at room temperature. It can be said that a high operating temperature is one of the characteristics of the single molecule SET reflecting the great size of the charging energy of the molecular Coulomb islands.

We also made molecular connections using C_{60} and oligothiophene nonamer, and observed (Fig. 12(a, b)) the Coulomb diamonds at a low temperature (11 K). Charging energy of over 100 meV and molecular vibration corresponding to the excited level were observed in both. However, the proportion of connections in which such SET characteristics could be observed unfortunately was only around a few percent of all the connections we made. The probability factor involved in the production process of devices is undoubtedly one of the reasons for this. For example, the width of the gaps between the nanogap electrodes that were formed under our experimental conditions were scattered over a range of a few to several tens of nanometers. It also remains unknown what kind of structures molecules form in bridging the gaps when they attach onto the surface of the electrodes. The fact that the molecules between the nanogaps are difficult to observe directly is also one of the major obstacles in the way of making improvements to the production conditions. Along with overcoming the issues pertaining to the production of the devices, appropriate molecular design is another important point. In the single molecule SET, the electrodes must essentially “inject” electrical charges into the molecules, but in actual molecular connections, the conductive electrons often permeate through the molecules to flow to the counter electrode. Among the porphyrin

molecular connections that we made, too, many of the molecules bridging the nanogaps were observed acting not as Coulomb islands, but as tunnel barriers^{[21][26]}. In these connections, the electrical charges injected into the molecules by the electrodes pass through to the counter electrode without passing along the molecular orbital. Clarifying the conditions under which injecting charges into molecules becomes possible is one of the major issues in molecular electronics going forward. In order to realize a “single electron device type” single molecule transistor, it will probably be necessary in terms of molecular design to control the connections with the electrodes, spatially isolate the π -conjugated system molecular orbitals, and set up a large density of states around the Fermi level to receive the conduction electrons.

3.3 The nanoparticle SET

Metal or semiconductor nanoparticles with diameters of a few to several tens of nanometers are relatively easy to synthesize through wet chemistry, and they can be obtained as solutions in which the nanoparticles of uniform diameter are dissolved. The various nanoparticle materials have been attracting attention as photonics materials that show unique optical properties, but they started to be used as components for nanoscale electronics devices from around 1996^{[27][28]}. In 1996, Kelin, et al., reported on a “nanoparticle SET” in which they bridged the gap between nanogap electrodes coated in wire-shaped molecules, with CdSe nanoparticles, to turn the nanoparticles into Coulomb islands and the wire-shaped molecules into the tunnel layer^{[17][29]}. Around the same time there were several reports on the characteristics of single electron transport in systems in which gaps between nanogap electrodes were bridges with single or small quantities of composite materials of monomolecular films and gold nanoparticles (GNP)^{[30][31]}. Recently, Majima, et al., demonstrated that the GNP-SET could be made with precision through a bottom-up process^[32]. They demonstrated the six types of logical operation (XOR, XNOR, NAND, OR, NOR, AND) using the GNP-SET with a double gate structure^[33], making great advances in production technology and duplicability.

Figure 13(b) shows the characteristics of the SET built using GNPs (of 6 nm in diameter) coated in an oligothiophene trimer (3T). Figure 13(a) is a SEM image of this device showing the two GNPs between the electrodes. This device is a double-dot SET in which these electrodes are joined in series to function as Coulomb islands. We will

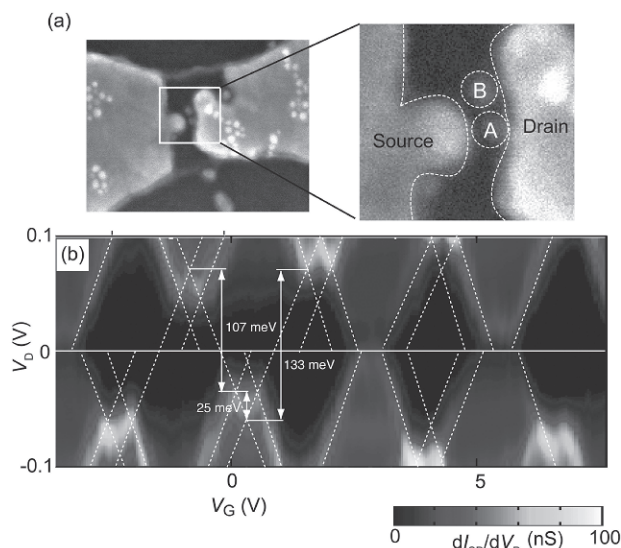


Fig. 13 (a): SEM image of GNP-3T hybrid SET (b): Coulomb diamond

not delve into the details, but it has been observed that a GNP potential in one area changes as the result of a GNP in another area becoming charged (this is seen in the 25 meV potential shift in Fig. 13(b))^[34]. The charging energy estimated from its properties is around 100 meV in both GNPs, and they are in good agreement with values expected from the diameter of the GNPs. 3T has thiol groups on both ends of the molecule, and it functions as a tunnel layer connecting the source and drain electrodes with the nanoparticles. Alkanedithiol has been used as the tunnel layer in many nanoparticle SETs reported to date, but this device is characterized by its extreme conductance (around 100 times that of similar devices that use alkanedithiol^[32]) reflecting the high electron transmissivity of the π -conjugated system molecules. These results suggest that the characteristics of the device such as its on-off ratio, signal to noise ratio, operational speed, etc., may be improved through the use of π -conjugated system molecules in the nanoparticle SET. Furthermore, as a result of the large tunnel conductance of the molecular wire in this system, interesting electrical conduction phenomena were observed such as cooperative effects in inelastic tunneling^[34], but we will not discuss them in this paper.

In addition, these nanoparticles mutually joined to form a network of their own accord. We ascertained that in one-dimensional networks in which the GNPs are aligned in a row, more activation energy (charging energy) is required for charge transfer between the GNPs because the electrostatic capacity formed by the GNPs becomes less than when one nanoparticle is sandwiched in the nanogap^[35]. It is hoped that making use of this will allow

development of SETs that operate at higher temperatures, and multiple-dot, single electron devices with advanced functions.

3.4 Photoirradiation switching SETs

Hybrid materials that consist of nanoparticles and organic molecules have the advantage of being easy to give organic molecule functions to nanometer sized materials. We measured the photoinduced discontinuous changes in current in the SET using a hybrid material consisting of molecules and GNPs around an oligothiophene frame. The structure of the SET is the same as before, so the details will be omitted. Clear Coulomb diamonds were observed through voltage mapping of each gate dI/dV_{SD} , and it was confirmed that the hybrid material is functioning well as an intermediate electrode.

This sample was irradiated with UV light ($\lambda < 450$ nm), and the current was measured at the same time (Fig. 14). The current was stable during non-irradiation, but when the sample was irradiated with UV light, the current instantaneously changed from 2.0 nA to 2.7 nA. The high current value was maintained even after irradiation stopped. When it was irradiated with UV light again, the current remained at 2.7 nA for around 10 seconds, after which it dropped suddenly to 1.5 nA. The current value remained at 1.5 nA even after irradiation stopped. This phenomenon was observed in other samples made by the same method, and it is highly duplicable. When samples were irradiated with UV light for several thousand seconds, around 10 sudden changes in the current were consistently observed. We believe these discontinuous changes in the current are based on changes at the single molecule level. This is because if they are based on changes in multiple

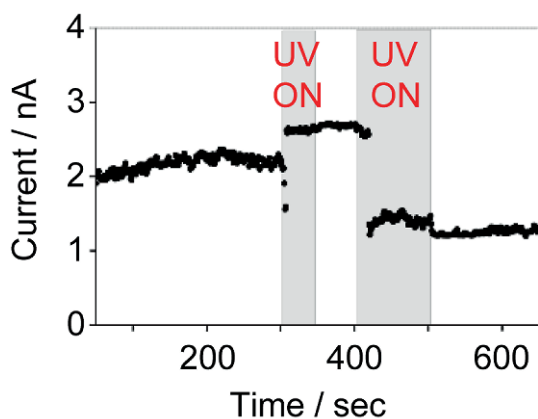


Fig. 14 Changes in the current upon irradiation with UV light. $V_{SD} = 50$ mV, $V_G = 0$ V. Time of irradiation with UV light is shown in grey.

molecules, the changes in current would be continuous.

We also examined the dependence of this phenomenon on the strength of the irradiation. The photoreaction was not observed with weak irradiation (0.032 mW/cm²), but the cycles of changes in the current increased dramatically with strong irradiation (1.3 mW/cm²). The digital-type changes in the current were not observed when samples were irradiated with monochromatic light with a wavelength of 520 nm. The reason for this was because single oligothiophene molecules do not absorb light with a wavelength of 520 nm, and GNPs show strong plasmon absorption. For this reason, the sudden changes in current under UV light irradiation are believed to be due to electronic excitation of the oligothiophene molecules.

To investigate the mechanism behind these digital-type changes, we measured the $I-V_{SD}$ of each gate voltage before and after irradiation (Fig. 15). An important change was observed in the shape of the $I-V_{SD}$ curve after photoirradiation. It was shown that the slope of the $I-V_{SD}$, dependent on the conductance of the oligothiophene molecules between the electrodes and nanoparticles, barely changes with photoirradiation. However, the threshold voltage of the Coulomb blockade (V_{Th}) was shown to change. This reveals that this phenomenon of a sudden change in the current is not due to a change in the connections between molecules, but it is the result of a change in the energy level of the Coulomb island, controlled by the gate voltage.

As a quantitative evaluation of the effect of

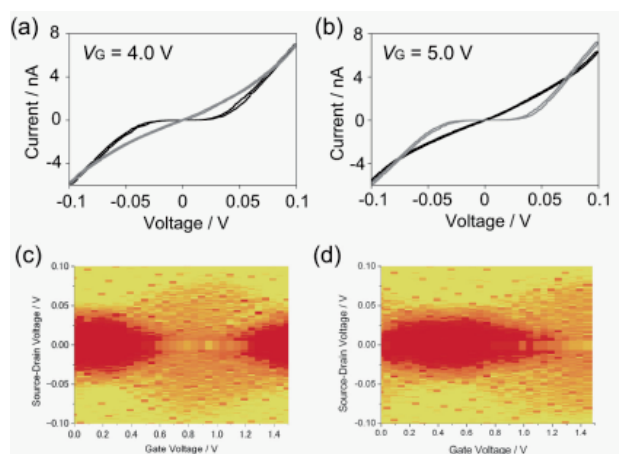


Fig. 15 The $I-V_{SD}$ characteristics at different gate voltages. The black lines in the diagrams at the top show the curve before irradiation with UV light, and the grey lines after irradiation (a): $V_G = 4.0$ V (b): 5.0 V. The diagrams on the bottom show the dI/dV_{SD} mapping before and after irradiation with UV light (c) and (d): After irradiation. The differential conductance is shown on a color scale ranging from dark red (0 nS) to bright yellow (100 nS).

photoirradiation, we compared differential conductance maps before and after photoirradiation (Fig. 15(c, d)). Before irradiation, two diamond structures were observed at $V_G = 0 - 1.5$ V. Only one diamond was observed after irradiation. The capacitance and charging energy of the connections are almost the same before and after irradiation. This result is characterized by the conductance and capacitance of the tunnel barrier, and the initial state of the SET is shown to remain unchanged by the photoirradiation. Rather, the photoirradiation changes the potential of the Coulomb islands, or in other words the positions of the Coulomb diamonds. From these results, it was ascertained that the reason for the sudden change in current due to photoirradiation is not Plasmon excitation of the GNPs, but it is due to changes in the oligothiophene molecules.

This SET made of hybrid material has (open end) molecules stuck to GNPs on one end only. One type of molecule bridges the gap between electrodes and GNPs, but because the conductance and capacitance of the tunnel barriers were not affected by photoirradiation, it was shown that these molecules did not change under photoirradiation. The other type of molecule has one end of the (open end) molecules stuck to GNPs. The conductance of open end molecules barely affects the conductance of connections. However, structural changes in these molecules disturb the potential of the GNPs. Because the conductance of connections changes little with photoirradiation, it is thought that the digital-type change in the current is caused by the structural change in open end molecules. From the fact that these sudden changes in the current are observed with greater frequency with an increase in the photoirradiation time, we believe that the changes in the current are caused by reversible changes in individual molecules. The exact nature of these molecular changes is as yet unknown, but the most likely reason is a change in polarization due to a change in the shape of the molecule^[36].

4 Conclusions

In the first half of this paper, we reported on the results of our research into the building of organic-inorganic hybrid photonic devices combining single molecule systems with photonic crystals. Using the new devices we proposed, we demonstrated for the first time that it is possible for single molecules to efficiently utilize light by making use of the integration of light and photonic crystal

modes, and that it is possible to control the fluorescence lifetime of single molecules using controlled nano radiation fields. These experiments clarified that the location and orientation of a single molecule on the photonic crystal is vital to the efficient utilization of light by the molecule and for controlling the emission of the molecule. By implementing a variety of molecule positioning and manipulation technologies in combination with the technology we developed in this research, we are one step closer to realizing a single molecule photonic device that can manipulate light at the single photon level.

In the latter half of this paper, we reported mainly on the results of our research on single molecule electronic devices, and in particular, devices that make use of the characteristics of single electric charge transport. The single molecule SET allows an extremely large charging energy, giving it the potential to be operated at room temperature, or the potential to be developed into unique devices that make use of the functionality of molecules, but we have yet to achieve greater duplicability. More work is needed to boost production technology such as ways of building nanogap electrodes and bridging the gap with molecules. At the same time, more research is needed on issues such as how charge injection from the electrode to the molecule is achieved and under what kind of conditions. The technology for building and duplicating the nanoparticle SET has been improving in recent years. If the operating temperature and yield rate is further improved, it has the potential to become a practical device. Furthermore, by utilizing the functionality of single molecules, it may become possible to draw out the full potential of the SET's high functionality. We are currently aiming to further boost the functionality of the SET through optimization of its structure including the molecules. The diversity of molecular devices will expand further if we focus on utilizing the functionality of molecules at the single molecular level, instead of only focusing on molecular joining. We have great expectations for the spread of molecular materials in nanoelectronics, and for it to contribute in the future to energy-saving, as well as to the development of highly functional next-generation devices.

Acknowledgments

We express our gratitude to Assistant Professor Syoji ITO (Osaka University) and Professor Hiroshi MIYASAKA (Osaka University) who provided the samples for the research reported on in the first half of this paper.

The research reported on in the latter half of this paper is joint research being carried out with Yutaka NOGUCHI (Chiba University). The research on molecular joining of porphyrin derivatives is being carried out jointly with Takashi NAGASE of Osaka Prefecture University. The research on the SET using a nonamer and GNP/3T is being carried out jointly with Michio M. MATSUSHITA (Nagoya University). The research on the photoreactive SET is being carried out jointly with Eiyu YAMAGUCHI (Kyushu University) and Kenji MATSUDA (Kyoto University). We would also like to thank all others involved.

References

- 1 B. Lounis and W. E. Moerner, "Single Photons on Demand from a Single Molecule at Room Temperature," *Nature*, Vol. 407, pp. 491-493, 2000.
- 2 Y. L. A. Rezus, S. G. Walt, R. Lettow, A. Renn, G. Zumofen, S. Götzinger, and V. Sandoghdar, "Single-Photon Spectroscopy of a Single Molecule," *Phys. Rev. Lett.*, Vol. 108, pp. 093601, 2012.
- 3 W. E. Moerner and L. Kador, "Optical Detection and Spectroscopy of Single Molecules in a Solid," *Phys. Rev. Lett.*, Vol. 62, pp. 2535-2538, 1989.
- 4 M. Orrit and J. Bernard, "Single Pentacene Molecules Detected by Fluorescence Excitation in a *p*-Terphenyl Crystal," *Phys. Rev. Lett.*, Vol. 65, pp. 2716-2719, 1990.
- 5 J. Hofkens, M. Maus, T. Gensch, T. Vosch, M. Cotlet, F. Köhn, A. Herrmann, K. Müllen, and F. De Schryver, "Probing Photophysical Processes in Individual Multichromophoric Dendrimers by Single-Molecule Spectroscopy," *J. Am. Chem. Soc.*, Vol. 122, pp. 9278-9288, 2000.
- 6 M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, and T. Kawai, "A Digital Fluorescent Molecular Photoswitch," *Nature*, Vol. 420, pp. 759-760, 2002.
- 7 A. Kinkhabwala, Z. Yu, S. Fan, Y. Avlasevich, K. Müllen, and W. E. Moerner, "Large Single-Molecule Fluorescence Enhancements Produced by a Bowtie Nanoantenna," *Nat. Photonics*, Vol. 3, pp. 654-657, 2009.
- 8 T. Kaji, T. Yamada, R. Ueda, X. Xu, and A. Otomo, "Fabrication of Two-Dimensional Ta₂O₅ Photonic Crystal Slabs with Ultra-Low Background Emission toward Highly Sensitive Fluorescence Spectroscopy," *Opt. Express*, Vol. 19, pp. 1422-1428, 2011.
- 9 T. Kaji, T. Yamada, R. Ueda, and A. Otomo, "Enhanced Fluorescence Emission from Single Molecules on a Two-Dimensional Photonic Crystal Slab with Low Background Emission," *J. Phys. Chem. Lett.*, Vol. 2, pp. 1651-1656, 2011.
- 10 T. Kaji, T. Yamada, S. Ito, H. Miyasaka, R. Ueda, S. Inoue, and A. Otomo, "Controlled Spontaneous Emission of Single Molecules in a Two-Dimensional Photonic Band Gap," *J. Am. Chem. Soc.*, Vol. 135, pp. 106-109, 2013.
- 11 A. Aviram and M. A. Ratner, "Molecular Rectifiers," *Chem. Phys. Lett.*, Vol. 29, pp. 277-283, 1974.
- 12 Edited by F. L. Carter, "Molecular Electronic Devices II," Marcell Dekker, New York, 1989.
- 13 C. Joachim, J. K. Gimzewski, and A. Aviram, "Electronics using hybrid-molecular and mono-molecular devices," *Nature*, Vol. 408, pp. 541-548, 2000.
- 14 Edited by H. Grabert, and M. H. Devoret, "Single Charge Tunneling: Coulomb Blockade Phenomena in Nanostructures (NATO Science Series B: Physics)," Springer, 1992.
- 15 Yasuo Takahashi, "Integrated Circuits Made of Silicon Single-Electron Devices," *OYO BUTURI*, Vol. 77, pp. 281-285, 2008. [in Japanese]
- 16 H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, "Nanomechanical Oscillations in a Single-C60 Transistor," *Nature*, Vol. 407, pp. 57-60, 2000.
- 17 D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, and P. L. McEuen, "A Single-Electron Transistor Made from a Cadmium Selenide Nanocrystal," *Nature*, Vol. 389, pp. 699-701, 1997.
- 18 T. Kubota, H. Hasegawa, and S. Mashiko, "Fabrication of Single-Molecular Device and Conductive Molecular Nanowire," *OYO BUTURI*, Vol. 75, pp. 0327-0331, 2006. [in Japanese]
- 19 J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yalsh, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abrunga, P. L. McEuen, and D. C. Ralph, "Coulomb Blockade and the Kondo Effect in Single-Atom Transistors," *Nature*, Vol. 417, pp. 722-725, 2002.
- 20 D. R. Strachan, D. E. Smith, D. E. Johnston, T.-H. Park, Michael J. Therien, D. A. Bonnell, and A. T. Johnson, "Controlled Fabrication of Nanogaps in Ambient Environment for Molecular Electronics," *Appl. Phys. Lett.*, Vol. 86, pp. 043109-1-3, 2005.
- 21 Y. Noguchi, "Fabrication of Transistor-Type Molecular Junctions and Their Charge Transport Properties," *OYO BUTURI*, Vol. 79, pp. 1014-1018, 2010. [in Japanese]
- 22 Y. Ono, A. Fujiwara, K. Nishiguchi, H. Inokawa, and Y. Takahashi, "Manipulation and Detection of Single Electrons for Future Information Processing," *J. Appl. Phys.*, Vol. 97, pp. 031101-1-19, 2005.
- 23 A. A. Houck, J. Labaziewicz, E. K. Chan, J. A. Folk, and I. L. Chuang, "Kondo Effect in Electromigrated Gold Break Junctions," *Nano Lett.*, Vol. 5, pp. 1685-1688, 2005.
- 24 P. Stein, A. Ulman, and T. G. Spiro, "Resonance Raman Spectra of S2TPP, SSeTPP, Se2TPP, and H2TPP: Extended Tetraphenylporphine Vibrational Assignments and Bonding Effects," *J. Phys. Chem.*, Vol. 88, pp. 369-374, 1984.
- 25 Y. Noguchi, R. Ueda, T. Kubota, T. Kamikado, S. Yokoyama, and T. Nagase, "Observation of Negative Differential Resistance and Single-Electron Tunneling in Electromigrated Break Junctions," *Thin Solid Films*, Vol. 516, pp. 2762-2766, 2008.
- 26 Y. Noguchi, T. Nagase, R. Ueda, T. Kamikado, T. Kobota, and S. Mashiko, "Fowler-Nordheim Tunneling in Electromigrated Break Junctions with Porphyrin Molecules," *J. J. Appl. Phys.*, Vol. 46, pp. 2683-2686, 2007.
- 27 A. Z. Zabet-Khosousi and A. -A. Dhirani, "Charge Transport in Nanoparticles Assemblies," *Chem. Rev.*, Vol. 108, pp. 4072-4124, 2008.
- 28 T. Sugawara and M. M. Matsushita, "Spintronics in Organic π -electronic Systems," *J. Mater. Chem.*, Vol. 19, pp. 1738-1753, 2009.
- 29 D. L. Klein, P. L. McEuen, J. E. B. Katari, R. Roth, and A. P. Alivisatos, "An Approach to Electrical Studies of Single Nanocrystals," *Appl. Phys. Lett.*, Vol. 68, pp. 2574-2576, 1996.
- 30 T. Sato, H. Ahmed, D. Brown, and B. F. G. Johnson, "Single Electron Transistor Using a Molecularly Linked Gold Colloidal Particle Chain," *J. Appl. Phys.*, Vol. 82, pp. 696-701, 1997.
- 31 A. Bezryadin, C. Dekker, and G. Schmid, "Electrostatic Trapping of Single Conducting Nanoparticles Between Nanoelectrodes," *Appl. Phys. Lett.*, Vol. 71, pp. 1273-1275, 1997.
- 32 N. Okabayashi, K. Maeda, T. Muraki, D. Tanaka, M. Sakamoto, T. Teranishi, and Y. Majima, "Uniform Charging Energy of Single-Electron Transistors by Using Size-Controlled Au Nanoparticles," *Appl. Phys. Lett.*, Vol. 100, pp. 033101-1-3, 2012.
- 33 K. Maeda, N. Okabayashi, S. Kano, S. Takeshita, D. Tanaka, M. Sakamoto, T. Teranishi, and Y. Majima, "Logic Operations of Chemically Assembled Single-Electron Transistor," *ACS Nano*, Vol. 6, pp. 2798-2803, 2012.
- 34 Y. Noguchi, T. Terui, T. Katayama, M. M. Matsushita, and T. Sugawara, "Super-Periodic Conductance in a Molecularly Wired Double-Dot System Self-Assembled in a Nanogap Electrode," *J. Appl. Phys.*, Vol. 108, pp. 094313-1-5, 2011.
- 35 Y. Noguchi, T. Terui, T. Katayama, M. M. Matsushita, and T. Sugawara, "Charge Transport in Various Dimensions of Small Networks Composed of Gold Nanoparticles and Terthiophene Wire-Molecules," *Appl. Phys. Lett.*, Vol. 98, pp. 263114-1-3, 2011.
- 36 F. Nishiyama, K. Ogawa, S. Tanaka, and T. Yokoyama, "Direct Conformational Analysis of a 10 nm Long Oligothiophene Wire," *J. Phys. Chem. B* Vol. 112, pp. 5272-5275, 2011.



Takahiro KAJI, Dr. Eng.

Researcher, Nano ICT Laboratory, Advanced
ICT Research Institute
Laser Photochemistry, Single-Molecule
Spectroscopy, Nanophotonics
kaji@nict.go.jp



Toshifumi TERUI, Dr. Sci.

Pranning Manager, Strategic Planning Office,
Strategic Planning Department
Condensed Matter Physics, Thin film.
Scanning Probe Microscope, Nano Electron
Physics
terui@nict.go.jp



Toshiki YAMADA, Dr. Eng.

Senior Researcher, Nano ICT Laboratory,
Advanced ICT Research Institute
Organic Materials, Material Physics,
Optical Measurement, Nano Materials
toshiki@nict.go.jp



Rieko UEDA

Technical Expert, Nano ICT Laboratory,
Advanced ICT Research Institute
Nanostructure Fabrication
urieko@nict.go.jp



Shin-ichiro INOUE, Ph.D.

Senior Researcher, Nano ICT Laboratory,
Advanced ICT Research Institute
Optoelectronics, Nanolithography, Organic
Nonlinear Optics, Nano-Photonic Devices
s_inoue@nict.go.jp



Akira OTOMO, Ph.D.

Director, Nano ICT Laboratory,
Advanced ICT Research Institute
Nanophotonics, Nonlinear Optics
akira_o@nict.go.jp