

Toward Bottom-Up Molecular Devices from the Self-Assembly of Tailored Molecules

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Abstract

We describe in this paper our attempts toward the development of “molecular devices”. The devices are fabricated based on chemical synthesis of molecules incorporating not only electronic and photonic properties but programmed information for higher organization as well. These molecules assemble themselves into elaborate superstructures that perform as devices such as light harvesting antenna and stimulus-responsive switches for electronic processes. Surface immobilization of molecules in arrangements defined at the molecular level may bring the endeavor a step closer to the realization of functional molecular devices.

1 Introduction

Almost exactly half a century ago, Richard Feynman gave a legendary lecture entitled “There is Plenty of Room at the Bottom” in a meeting of the American Physical Society [1]. In the lecture, he raised a question such as “what are the limitations as to how small a thing has to be before you can no longer mold it?” and discussed possibilities of making the smallest computers and the smallest machines. Fifty years later, nanoscience and nanotechnology have become one of the most actively studied subjects in the world.

The molecule, which is formed from atoms that covalently bind each other, is the minimum unit that can exhibit a nontrivial function. If one can make a computer from molecules, in which individual molecules function as memories, gates, wires, and so on, it would be the smallest computer that one can imagine. If one can make a machine from molecules, in which individual molecules function as gears, motors, cylinders, and so on, the machine would be the smallest conceivable. Herein I present our attempts in the early stages to create molecule-based computers and machines—molecular devices—in the early stages toward the futuristic goal.

2 Metal Complex-based Molecular Switches

Studies on the manipulation of electrons and photons at the molecular or supramolecular level may lay the foundation for potential applications in

molecular photonic and electronic devices [2, 3]. For the device to work in a cooperative fashion, communication between each component is critical. Electron and energy transfer processes may serve as the means of information transmission among molecules. Further, switching of the signal transmission is needed to perform logic operations. Metal complexes have some advantages for use in electronic and photonic processes, because many of them exhibit favorable electronic and photonic properties, such as accessible redox potentials, excited energies that correspond to visible light, and excited state lifetimes long enough to effect subsequent electronic events.

The dinuclear ruthenium/osmium complex **RuOs** is a prototypical molecular switch in which its intramolecular energy transfer process is turned on upon electrochemical reduction [4]. Each of the metal centers is the well-known d^6 -metal tris(bipyridine) unit, which has been extensively studied in terms of photophysics and electrochemistry owing to its potential applications in energy conversion schemes. The azo-containing bridging ligand effectively deactivates the excited state of the metal complex and hence the luminescence is not observed from the complex. Upon one-electron or two-electron reduction, the electronic state of the azo-containing ligand changes in a way that interferes much less with the excited state of the metal complex. Thus, the processes expected for the parent d^6 -metal tris(bipyridine) complex are now activated, that is, the energy transfer from the ruthenium unit to the osmium unit, in this particular case.

Since the first discovery of the molecular switch, the study has been extended to various types of azopolypyridine-containing multinuclear metal

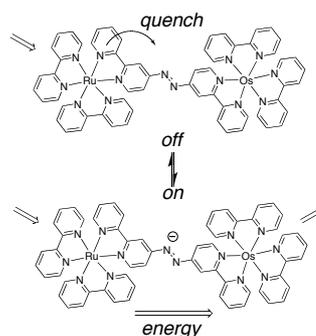


Figure 1: Molecular switch **RuOs** for energy transfer.

complexes that function as switches for energy transfer. The star-shaped multinuclear ruthenium/osmium complex **Ru₃Os** is among the most recent entities [5]. Since the absorptivity of the complex is large owing to the presence of three ruthenium units, it works as a first example of a switchable antenna, although it is unfortunate that the clear switching phenomenon resulting in the luminescence from the central osmium unit occurs only at a low temperature. The photophysical processes has been examined with the state-of-the-art femtosecond transient absorption spectroscopy.

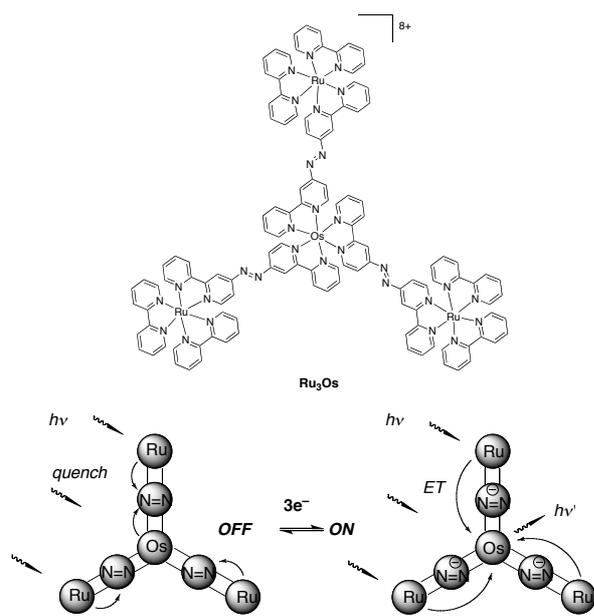


Figure 2: Switchable antenna **Ru₃Os**.

3 Supramolecular Electron/Energy Transfer and Their Switching

It may not be realistic to put increasingly complex functions all into one molecule, because required molecular structure may become too complicated beyond reasonable synthetic effort. Molecules incorporating programmed information for higher organization may assemble themselves into well-defined supramolecules [6]. Directional noncovalent intermolecular interactions, such as hydrogen bonding and coordination interaction, incorporated into photo/electroactive building blocks may be exploited to direct the formation of photo/electroactive supramolecules that may perform complex functions that may not be possible within a single molecule.

The most popular motif in this context is a photosensitizer–electron acceptor dyad bridged by an appropriate intermolecular bond. The extension of this approach to assemble multiple components may produce light-harvesting antenna. We have prepared the porphyrin pentad

consisting of four zinc porphyrins surrounding a free-base porphyrin located in the center, as shown in Figure 3 [7]. These porphyrin molecules are bridged by amidinium–carboxylate salt bridges, which are double hydrogen bonds augmented by the electrostatic interaction via the charge pair. The light energy absorbed by one of the peripheral zinc–porphyrins is collected in the central free-base porphyrin. The rate of energy transfer has been found to be $1.2 \times 10^{10} \text{ s}^{-1}$ and the quantum yield of this process amounts to near unity, 0.96. The rate of energy transfer is faster than predicted from the through-space mechanism, which is usually assumed for supramolecular energy transfer. We have proposed that the through-bond mechanism operates in the electronic excited energy transfer process on the basis of comparative time-resolved measurements for related supramolecules [8].

Switching of electronic processes have also been realized in supramolecular systems. A photochromic stilbazole unit has been incorporated into the bridge in a donor–bridge–acceptor scaffold constructed via a coordination interaction as in Figure 4 [9]. The

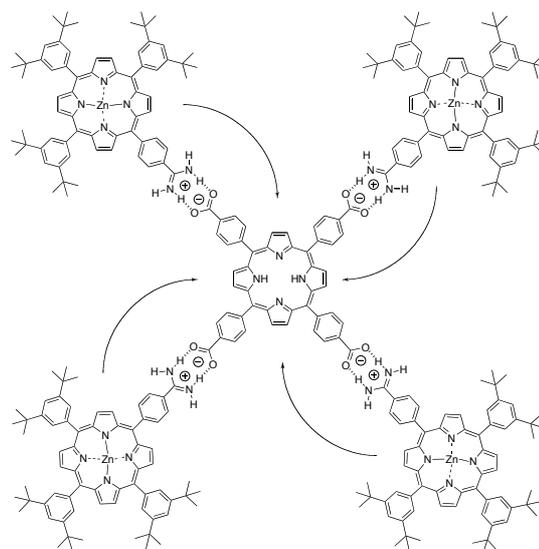


Figure 3: Supramolecular light-harvesting antenna **Zn₄Fb**.

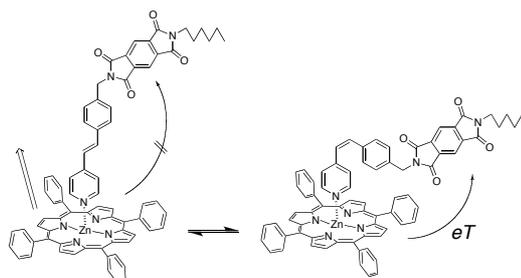


Figure 4: Supramolecular switch for electron transfer.

carbon–carbon double bond isomerizes upon photoirradiation. An efficient electron transfer occurs for the cis isomer of the bridge whereas no electron transfer is detected for the trans isomer. The electron transfer rate (k_{et}) and efficiency (Φ_{et}) for the cis complex are determined as $1.83 \times 10^9 \text{ s}^{-1}$ and 0.77, respectively.

3 Surface Supramolecular Chemistry

The molecular electron/energy transfer and switching devices thus far described work in homogeneous solutions. Constructing supramolecules on surfaces, on the other hand, is an important and challenging theme in view of connecting molecular assemblies to the macroscopic world for potential applications in the field of molecular devices. Scanning tunneling microscopy (STM) provides chemists a unique opportunity to observe individual molecules in real space, once the molecules are immobilized on a surface. Highly oriented pyrolytic graphite (HOPG) is a convenient substrate for this purpose, though it might not be appropriate in applications as is, because it is stable under atmosphere and an atomically flat surface is easily obtained. Thus, molecules on HOPG surface are targets of many researches to obtain insight into what molecules arrange themselves into on an individual molecule basis. The knowledge obtained in these studies may then be utilized as design guides in the construction of molecular architecture with desired structures.

Figure 5 shows a STM image taken at the interface of HOPG and a solution containing the porphyrin derivative having two carboxyl moieties [10]. The STM reveals that a hydrogen bonding network between the carboxyl moieties gives rise to the lamellar pairwise arrangement. It has also been revealed that porphyrin molecules incorporating directional intermolecular interaction sites in different symmetries affords new surface patterns accordingly.

Now we want to extend this approach to 3D. Vertical extension of the two-dimensional (2D) order, if achieved, would provide a powerful methodology to produce well-defined 3D architectures on surfaces. One approach is to use the axial coordination to metal porphyrins. We have reported for the first time on the observation of labile axial coordination at a liquid/solid interface [11]. In the experiments, we first observed a mixed solution of zinc-tetraphenylporphyrin and free-base tetraphenylporphyrin. These two porphyrins could hardly be differentiated with STM. 4-Phenylazopyridine was then added to this solution. As displayed in Figure 6, some of the porphyrin

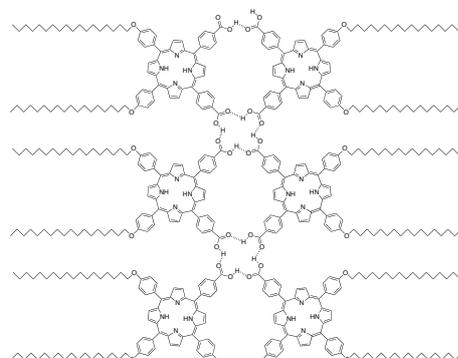
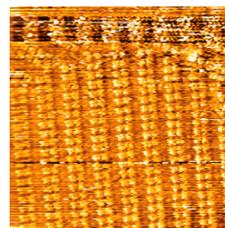


Figure 5: STM image ($50 \times 50 \text{ nm}^2$) and schematic arrangement of the hydrogen-bonding porphyrin derivative self-assembled at the HOPG/1-phenyloctane interface.

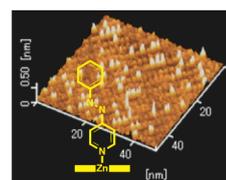


Figure 6: STM image for molecular pillars on ordered bases.

exhibited much higher protrusions than others, which is indicative of the selective binding of the axial ligand to the zinc-porphyrin. With this experiment, it has become clear that a labile ligand can be observed with STM. Further, statistical analysis revealed that the *trans*-phenylazopyridine and *cis*-phenylazopyridine give different contrasts in the STM images. More importantly, it has become clear that molecules can be put on highly ordered basal molecular (porphyrin) arrays. In other words, we can put up molecular pillars on an array of molecular bases, which could be used to construct 3D supramolecular architecture on a surface.

In addition to molecule-based electronic components, mechanical components can be envisaged. Double decker compounds are a class of compounds in which a lanthanide ion is sandwiched between two macrocyclic rings, such as porphyrins and phthalocyanines. The two macrocyclic rings may rotate at variable rates depending on the central metal ions and substituents on the macrocycles. We noted that if one of the macrocyclic ligands is immobilized on the surface, the other ring—now the upper ring—may rotate with respect to the surface, which could be detected with STM with the molecular

resolution. We have prepared several double decker derivatives and investigated their arrangements at the liquid/HOPG interface. Figure 7 shows a STM image for the molecule shown by the image [12]. Each one of the elliptic bright spots in the STM image is consistent with the oblong shape of the upper ring. It is therefore concluded that the long axes of the upper rings lie perpendicular to the molecular rows. Variable temperature ^1H NMR studies on this molecule in a homogeneous solution suggested that the two rings change orientation by 90° with respect to each other about three times per second at room temperature. Since it takes several seconds to complete the image for a single molecule in this particular image in our scanning conditions, it is possible for the molecules to be rotating many times during the image acquisition. The studies on the rotational motion on the surface is in progress. These works may lead to the development of molecular gears, if cooperative rotational motion is realized on the surface just as macroscopic gears that mesh with one another.

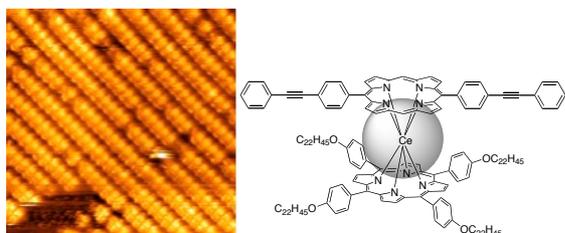


Figure 7: STM image ($50 \times 50 \text{ nm}^2$) for the double decker porphyrin.

4 Conclusion

Herein we first described our attempts toward the development of molecular devices that perform electronic and photonic functions in solutions. Although the processes are certainly taking place within each single supramolecule, the observation is necessarily on the ensemble of a large number of molecules on the order of Avogadro's number. Surface supramolecular chemistry opens a new stage for the development of molecular devices, because observation of individual molecules in real space is now possible. Further, the surface organization may allow molecules to communicate with each other not only by electronic means but mechanically. The dream of Richard Feynman is coming closer a little bit and will come true for sure along the road ahead.

References

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