From Gas Phase Clusters to Nanomaterials: An Overview of Theoretical Insights

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Since theoretical investigations of gas phase clusters enable the evaluation of intrinsic molecular properties and intermolecular interactions, one can predict the macroscopic properties of bulk matter, from a microscopic determination of the properties of individual atoms, molecules, or clusters. Based on the insights obtained from theoretical investigations of the properties of a large number of cluster systems (ranging from simple water clusters to large π-systems), we have investigated the properties of various novel molecular systems including endo/exohedral fullerenes, nanotori, nonlinear optical materials, ionophores/receptors, polypeptides, enzymes, organic nanotubes, nanowires, and electronic and nano-mechanical molecular devices. The present mini-review highlights some of the interesting results obtained in the course of our extensive theoretical investigations of clusters and nanomaterials.

Key Words : Computer-aided molecular design, Molecular clusters, Ionophores, Nanotubes, Nanodevices

Introduction

During the last few decades, conventional host-guest molecular systems including supra-molecules with novel and exotic structures have been the focus of extensive investigations.[1] However, the practical exploitation of most of these systems requires a more detailed insight of the structure-function relationships. In this context, rigorous quantum chemical investigations have proven to be of value because in addition to aiding the understanding of such structure-function relationships, they can also be used in the de novo design of novel molecular systems and functional materials.

Given the ability of nano-chemistry to provide functional materials of practical utility in the near future,[2] the predictive power of quantum chemical calculations are of significant value because interesting individual molecules or small clusters can be developed as viable functional materials and devices. Interest in molecular level devices is also high because they aid the development of extremely small, fast, and powerful computers. Another area of interest has been the use of molecular recognition events as microscopic chemical/biochemical sensors/monitors such as DNA chips. It should be emphasized that most of the above research thrives on ideas gleaned from condensed matter physics, chemistry, computational science and biology.

Consequently, the prediction of properties of nanomaterials from a nanoscopic determination of the properties of individual atoms, molecules, or clusters, has begun to attract a lot of attention. Much of this interest stems from the utility of such studies in the design and development of novel functional nano-systems with potential applications in electronics, photonics, chemistry, biology, neuroscience and medicine, based on molecular interactions[3] (with ion/atom/molecule/electron/photon), molecular recognition,[1] nano-recognition,[4] molecular clustering/aggregation,[5] self-assembly,[1,6] and self-synthesis.[7] In this context, we have carried out detailed theoretical investigations of the properties of a large number of cluster systems, ranging from simple water clusters to large π-systems.

The intrinsic molecular properties and intermolecular interactions obtained from the gas phase clusters enable us to predict structures and properties of nanomaterials. Therefore, an effective design strategy would require a thorough understanding of various interaction forces and mechanisms. In this connection, we have theoretically characterized novel interaction forces. We have employed diverse theoretical methods ranging from traditional *ab initio*, density functional theory, tight binding, path-integral, Monte Carlo to molecular dynamics simulations. In the course of these investigations, we have been successful in elucidating the properties of a diverse range of novel molecular systems. These include molecular clusters (water clusters,[8] solvated cations,[9] solvated anions,[10] solvated electrons,[11] solvated chemical compounds,[12] solvated biomolecules,[13] solvated surfaces,[14] inorganic/metal clusters[15]), endo/exhohedral fullerenes/nanotori,[16] nonlinear optical materials,[17] ionophores/receptors,[18,19] polypeptides/membranes,[20] enzymes,[21] organic species,[22] organic nanotubes/nanowires,[6,7] photo/electro-nanodevices,[23] and nano-mechanical molecular devices[24] (Fig. 1).

The success of our design strategy is validated by our experimental characterization of novel ionophores,[19] organic nanotubes,[7] and molecular flippers[24] as well as many other experimental demonstration[25] by other groups. For example, we have designed receptors with high affinity and selectivity for specific cations (acetylcholine, NH_4^+) or anions (F^-, Cl^-) which are biologically important.[19] Quantum nanostructures have been synthesized.[6,7] Our designed photo-electronic[23] and nano-mechanical[24] molecular devices would be useful for computer memory with nonlinear optical switch phenomena and molecular vehicles/tweezers for drug delivery and

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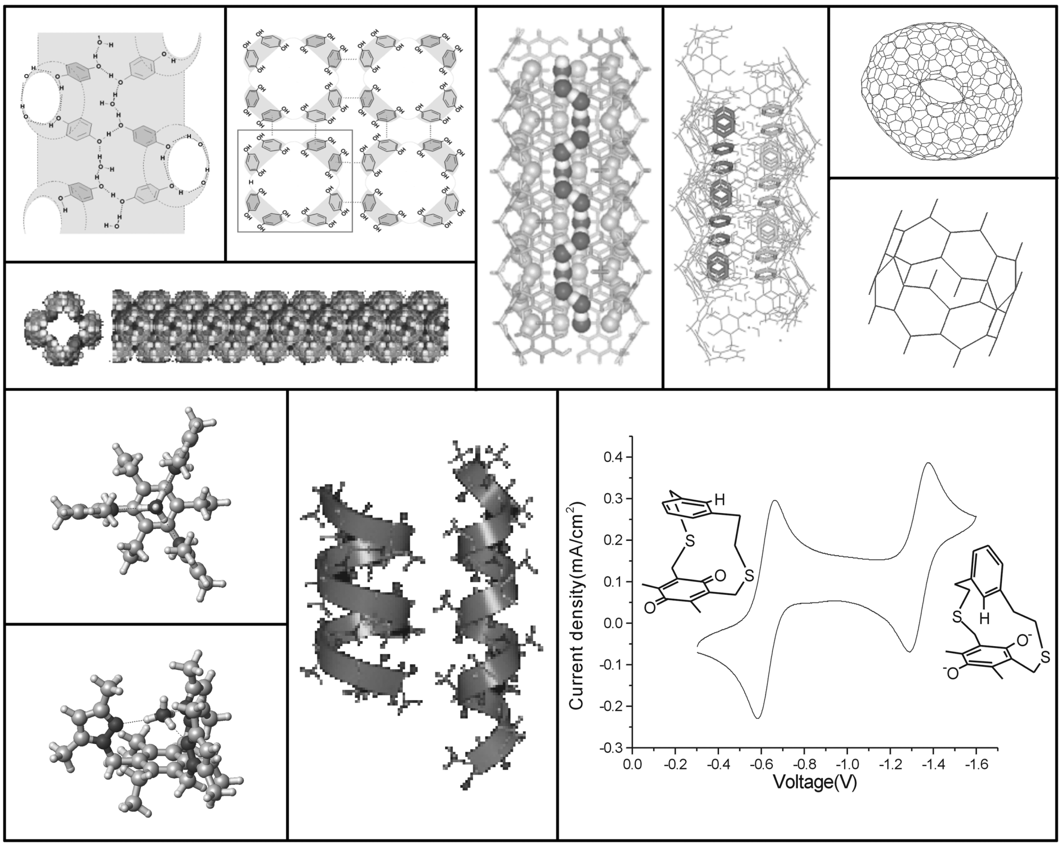

Figure 1. Organic nanotubes (one dimensional H-bonds relays and displaced π–π stacks); nanotorus, beltenes, ionophores/receptors, and left-handed lambda *vs* right-handed alpha helices, and molecular flipper.

nano-surgery, respectively. In the course of this review, we elaborate on the theoretical accomplishments which eventually led to the de novo design of these novel functional molecular systems.

Molecular Clusters and Interaction Forces

Studies of carbon clusters, oxygen/sulfur clusters, metal clusters would provide the intrinsic properties of these clusters.[15,16] We find that endohedral fullerenes (by the presence of N, P, As, O, S)[16d] would be useful for quantum computing due to the presence of isolated and controllable spins. We have demonstrated the unusual magnetic phase transition in exohedral fullerenes.[16b] Structures, energetics, and electronic structures of carbon nanotubes have been investigated,[16c] and the (3, 3) carbon nanotubes have recently been characterized. We also investigated the smallest building blocks of carbon nanotubes: trannulenes, cyclacenes, collarenes.[18f] These species have shown very intriguing electronic properties of singlet-triplet degeneracy and insulator-to-semiconductor transitions with the increase of molecular size. We have also predicted the structures and electronic properties of smallest nanotori, which show interesting metal, semiconductor, and insulator characteristics depending on nanotube building blocks.[16c]

The clusters composed of inorganic atoms often show interesting properties. We have investigated highly energetic oxidants, O_n clusters, which have been compared with S_n clusters.[15] O_4 is found to be the highest energetic oxidant among O_n clusters.

The information of intermolecular interactions can be obtained from the studiy of molecular clusters. The hydrogen bonding would be one of the most important interactions in biosystems. The most typical case is the water clusters, since water is the universal constituent in biosystems, environments, atmosphere, and interstellar space. We have investigated the structures and energetics of water[8] and electron-water[11] clusters. All these structure have been verified to be correct by recent experiments.[25] Thus, the assembly phenomena based on hydrogen bonding are well understood. The electron-water clusters would be an important role in precloud chemistry. Thus, the structure and energetics of water clusters with an excess electron is important for understanding the thermodynamics of atmospheric chemistry. In particular, this understanding is critical to understand the solvation phenomena for the cation,[9] anion,[10] aromatic compounds,[12] and biomolecules.[13] Thus, we have reported these structures, thermodyamic quantities, and vibrational spectra in a series of papers. These predicted results have also been verified in many recent experiments.[25] All these basic forces in gas phase molecular clusters are found to be very useful in designing new functional molecular systems.

Design and Development of Functional Molecules, Nano Materials, and Nanodevices

Our aim is *ab initio* design and development of novel functional molecular systems through our understanding of molecular functional mechanisms and assemblies. In sharp contrast to conventional host-guest systems, the guests in our case include photons, electrons, and protons. To this end, we investigate the capabilities of manipulating individual photons/electrons/protons/atoms/molecules (for understanding the function in molecular devices/sensors) and the principles governing bio-molecular recognition, solvation mechanisms including proton exchange, signal transduction, knowledge recognition, and memory retention in living systems. For practical utility, we design novel molecular electronic/photonic devices and molecular sensors. These include single electron/photon devices and molecular tools to manipulate a single electron/photon. Some of predicted devices/sensors have been synthesized and characterized. We include the study of electron tunneling, proton tunneling, and current flow at the molecular level. Our planned approaches are as follows: (1) Designing novel superfunctional molecular systems through elucidation of host-guest interactions and molecular self-assembly/self-synthesis, (2) Designing electron/photon/proton-host systems and studying its capture/release /transfer mechanisms and dynamics, and (3) Designing nanodevices. All these aims have been successfully carried out. Firstly, novel types of interaction forces have been elucidated.[3] Secondly, the catalytic role of enzymes (in particular, the importance of electron dissipation and charge buffering) has been further clarified.[21] Thirdly, novel functional organic nanotubes and nanowires have been characterized.[6,7] Finally, novel ionophores[19] and nanomechanical devices[24] have been designed, synthesized, and characterized.

(i) Ionophores/receptors: Molecular level studies of intermolecular interaction forces and microscopic structures have been accomplished to understand molecular aggregates and self-assembly phenomena. The design and synthesis of receptors capable of binding anionic or cationic guests is of crucial importance due to its potential applications in environmental and biological processes. Based on this, we have been successful in designing and synthesizing various types of novel ionophores.

Utilizing our earlier work of the cation-π interactions,[18a-c] we investigated a new type of ionophore family of [n]beltenes.[18f,18k] We also recently designed, synthesized, and characterized tripodal cation ionophores/receptors.[19] In particular, acetylcholine receptors [1,3,5-tris(pyrrolylmethyl) benzene][19c] can aid the discoveries of novel drugs with understanding the binding mechanism.

Novel amphi-ionophores in gas phase and in aqueous solution have been designed for the first time.[18g,18l]

Tripodal receptors for halide anion binding have been designed and synthesized. These receptors show extremely high affinity and selectivity for F^- and Cl^-.[19a,19b] A tripodal receptor shows strong affinity and high selectivity for F^- through $(C\text{-}H)^+\text{---}X^-$ hydrogen bonds.[19b] Another type of tripodal receptors for halide anion binding has been designed and synthesized. These show extremely high affinity and selectivity for Cl^-.[19a] In this case, we employed both charge-charge interactions and charge-dipole interactions.

This approach would also aid design of novel functional molecular systems and biologically important chemosensors based on ion selective electrode.

(ii) Organic nanotubes and nanowires: Using the computer-aided molecular design approach, we recently reported the synthesis of calix[4]hydroquinone (CHQ) nanotube arrays[6] self-assembled with infinitely long one-dimensional (1-D) short hydrogen bonds (H-bonds)[4b] and aromatic-aromatic interactions.[26] For the design of the CHQ nanotubes and the study of their assembly process, we employed both chemistry approach (based on ab initio and density functional theories) and physics approach (based on first principles calculations using ultrasoft pseudopotential plane wave methods). Since X-ray structures do not contain the positions of H atoms, it is necessary to analyze the system using quantum theoretical calculations. The competition between H-bonding and displaced π–π stacking in the assembling process has been clarified. The IR spectroscopic features and NMR chemical shifts of 1-D short H-bonds have been investigated both experimentally and theoretically. The dissection of the two most important interaction components leading to self-assembly processes would help design new functional materials and nano-materials.

For the computer-aided molecular design strategy, on the basis of intermolecular interaction forces (*i.e.*, hydrogen bonding and aromatic-aromatic interactions), we investigated the assembling phenomena of CHQs with density functional calculations of various possible combinations of assembled structures derived from previously reported calixarene-based dimers, trimers, tertramers, hexamers, and polymers.[27] The results suggest that in the presence of bridging water molecules, a linear tubular polymeric structure is highly stabilized by the formation of H-bonded bridges between repeating tubular octamer units. These predicted organic nanotubes have been successfully synthesized.

After the synthesis and characterization of the nanotubes, we have further investigated the details of predicted assembly phenomena as well as the refined structure and electronic properties of the CHQ nanotubes.[4b] Based on our calculation results, we have clarified the origins of 1-D H-bonding and displaced π–π stacking in the assembling process and these competitions. The spectroscopic features of 1-D short H-bonds have been elucidated. These interesting structures and functions of the organic nanotubes would find various applications in chemistry, physics, and biology.

The crystal structures shows that the nanotubes have infinitely long 1-D H-bond arrays. The crystals can be grown into thick and long multi-channel bundles (up to 0.5 mm wide and 5 mm long). The crystal structure shows that the bundles of CHQ nanotubes form novel chessboard-like rectangular structures. Each nanotube has 17×17 Å^2 cross section with 8×8 Å^2 square pore (with the van der Waals volume excluded). Since the nanotubes are electrochemically and photochemically active, they should find numerous applications such as a model for selective water/ion channels in biological systems and a nano-host to include size-specific guest molecules.

Using these organic nanotubes as templates, we synthesized ultra-thin silver nanowire arrays. These could be applied as nanoconnectors for nanodevices.[7] First principles calculations suggest the existence of three conducting channels for electron transport as a quantum wire. The ultra-thin silver nanowires with infinitely high aspect-ratio would serve as model systems for investigating many exciting 1-D physical phenomena as well as nano-electronic devices.

The nanotubes arrays can be utilized in many interesting nanosystems. The redox reaction of the nanotube with novel metal ions allows to form silver nanowire arrays. The wires exist as uniformly oriented three-dimensional arrays of ultrahigh density, and thus could be employed as model systems for investigating one-dimensional phenomena and as nanoconnectors for designing nanoelectronic devices. Nanowires have attracted extensive interests in recent years because of their unusual quantum properties and potential use as nanoconnectors and nanoscale devices. To obtain enhanced physical properties, the wires need to be of small diameter and high aspect ratio, and to be uniformly oriented. The characterization of metal nanowires has been extended from silver to gold, platinum, palladium and mercury.

(iii) Catalytic residues in enzymatic reaction: We have investigated the role of catalytic residues in enzymatic mechanisms. Our previous research on enzymatic reaction mechanism[21b] has been expanded to have more generalized concept.[21d] In particular, the charge buffering/dissipation role has been clarified. We have detailed the structures of the active site of ketosteroid isomerase and the role of various catalytic residues, and have explained the origin of its fast reactivity by carrying out a detailed investigation of the enzymatic reaction mechanism. The catalytic residues, through short strong hydrogen bonds, play the role of charge buffer to stabilize the negative charge built up on the intermediates in the course of the reaction.

(iv) Left-handed helix of polypeptides: In polypeptides, we have first noted that the left-handed helix can exist, in contrast to the conventional wisdom of right handed helix.[20c] The diameter of the left-handed helix is larger than the conventional right-handed helix. The left-handed helix is stabilized when the terminal residues are charged, because the dipole moments of carbonyl groups for the former are aligned opposite to those of the latter. This indicates that the protein folding can be controlled by the charged moieties of either the polypeptides or the residues of other molecules around the terminal ends of the polypeptides.

(v) Nanomechanical device: A molecular flipper has been designed, synthesized, and characterized.[24] The flipping/flapping motion, which is due to the changes of edge-to-face and face-to-face aromatic interactions,[26] can be electrochemically controlled by reduction/oxidation of the quinone moiety in the molecular system. We believe that the present investigation would spur the development of novel nano-mechanical devices whose motion can be controlled through electrochemical means. The conformational change of the upper benzene ring in the normal state reduces to the dianionic state, upon accepting two electrons by voltage change. Thus, the conformational changes between reduced and oxidized states can be made very fast by electrochemical process.

Concluding Remarks

Utilizing the knowledge of molecular interactions obtained from the gas phase clusters, we have tried to design and synthesize functional molecular systems: nanowires/nanotubes, receptors/sensors, and molecular robotics. These would be eventually useful for molecular nano-electronic/mechanical devices, quantum computing devices, biomolecular sensors, and nano-surgery. Indeed, we have succeeded in synthesizing functional organic nanotubes which are composed of electrochemically and photochemically reactive functional groups. Using these organic nanotubes, we have made very long and thin silver nanowire arrays. Sub-nanowires can form super-crystalline structure with 3-dimensional arrays which are all coherently oriented atomwise. Other interesting metal wires are also formed inside the organic nanotubes in ambient experimental condition. For practical utility for nanodevices, we have characterized nanowires of gold, platinum, palladium, and mercury. Since these metals have their own characteristics, their utility would be interesting. In addition, we are also interested in designing ferromagnetic metal nanowires and superconducting nanowires.

Based on novel molecular interaction forces, we have also been successful in designing various receptors and ionophores, and in understanding the reaction mechanisms of enzymes. This research will be further expanded to include drug design. The knowledge of the novel interaction forces in functional molecular systems would be utilized for the development of bio-nano-robotics, such as molecular vehicles and electron/proton/molecular tweezers. Novel functional molecular systems could be designed so as to have the capacity of controlled assembling. Artificial receptors, bioinformatics, nano-sensors (including DNA chips), and bio-nano-robotics would be utilized to design novel drugs, to obtain genetic information, to examine illness, and to carry out local-surgery. These fields are still in embryo. We have been working on this project, based on computer-aided molecular design strategy for developing functional organic/bio-organic molecular systems. It is encouraging to note the worldwide progress of various kinds of research from molecular interactions to material/device-design.

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