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Creative Research Initiatives

초기능성 분자계의 설계와 개발 및 반응기능기작과 분자조립현상 연구

Design and Development of Superfunctional Molecular Systems and Study of their Functional Mechanisms and Molecular Assemblies

Center for Superfunctional Materials, Pohang University of Science and Technology

Ministry of Science & Technology

제 출 문

과학기술부 장관 귀하

본 보고서를 "Design and Development of Superfunctional Moleculear Systems and Study of their Functional Mechanisms and Molecular Assemblies 에 관한 연구"과제의 보고서로 제출합니다.

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요약(연구결과를 중심으로 개조식 500자이내) — 보고서 면수: 47

1. Various novel types of interaction forces responsible for diverse phenomena ranging from host-guest recognition and molecular assembly (self-assembly and self-synthesis) to chemical and enzymatic reactions have been characterized.
2. Novel ionophores/receptors have been designed, synthesized, and characterized.
3. Assembly phenomena including formation of molecular clusters and metal-alloy nano-clusters as well as solvation phenomena have been investigated.
4. The left-handed helix (λ-helix) in proteins has been first predicted.
5. The first nonlinear optical switch which can be controlled by laser was designed. This study is important in quantum optical information processing devices and sensors.
6. A first electrochemically controllable molecular nanodevice was designed and synthesized as a precursor of electrochemically-controllable molecular vessel, which could be utilized as as a means of drug delivery and nano-surgery.
7. Pysical properties of endohedral fullerines, metal nanoclusters and nanowires are predicted.
8. Functional organic nanotubes and coherently aligned metal sub-nanowires have been designed, synthesized, and characterized.

색 인 어 (각 5개 이상)	한 글	자기조립, 자기합성, 왼쪽나선헬릭스, 나노관, 나노선
	영 어	self-assembly, self-synthesis, left-hnaded helix, nanotubes, nanowires

요 약 문

Ⅰ. 제 목

초기능성 분자계의 설계와 개발 및 반응 기능기작과 분자 조립 연구 현상

Ⅱ. 연구개발의 목적 및 필요성

본 연구의 목적은 분자의 상호작용, 분자 조립, 전자나 광자및 양성자의 포획과 방출및 전달 기작과 동력학에 대한 해석, 유한 크기의 나노물질의 성질에 대한 연구를 통해 새로운 기능성 분자계을 설계하는 것이다. 새로운 기능성 분자계를 설계하고 개발하는 것은 나노 뭉치, 나노 관, 나노 선, 분자 선, 분자 기억장치, 분자 컴퓨터, 분자 운반체, 분자 로봇, 나노 전자소자 혹은 기계소자등과 같은 곳에 폭 넓은 응용성을 가질 것이다.

Ⅲ. 연구개발의 내용 및 범위

전통적인 host-guest system들과는 대조적으로, 본 연구에서의 guest는 광자, 전자, 또는 양성자도 포함하고 있다. 따라서 분자소자 및 감지기의 기능을 연구하기 위해 광자, 전자, 양성자, 원자, 이온및 분자를 조작할 수 있는 방법과 생체계에서의 생분자 인지, 용매화 기작, 신호 변환, 지식 인지, 및 기억을 통제하는 원리를 연구한다. 또한 실용적인 면에서 새로운 분자 전자소자 및 광소자와 분자 감지기를 개발한다.

Ⅳ. 연구개발결과

나노 인지, 자기 조립과 자기 합성의 개념을 기초로 하여 새로운 이온투과담체, 기능성 유기 나노 관, 상호간섭적으로 정렬된 금속 나노 선 및 전기화학적 통제가 가능한 나노 소자를 설계하고, 합성하고, 측정했다. 또한 단백질에서의 좌선형 helix (λ-helix)와 최초의 비선형 광 개폐기를 예측했다.

Ⅴ. 연구개발결과의 활용계획

Host-guest system, 분자 인지, 생분자의 구조 및 분자 조립에 관한 이해는 화학의 다양한 분야에 유용하다. 설계된 이온투과담체와 수용체, 나노 관과 나노 소자는 새로운 나노 감지기와 나노 물질 및 나노 소자를 개발하는데 있어서 매우 유용하다. 한편 나노 운반체와 같은 나노기계 소자는 의약의 운반 및 나노 수술을 위해 유용할 것이다.

S U M M A R Y

Ⅰ. Title :

Design and Development of Superfunctional Moleculear Systems and Study of their Functional Mechanisms and Molecular Assemblies

Ⅱ. Research Objective

The objective is to design novel functional molecular systems through elucidation of molecular interactions, molecular assemblies, electron/photon/proton capture/release/transfer mechanism/dynamics, and study of the properties of nanomaterials in finite dimensions. To design and develop novel functional systems would have widespread applications like nanoclusters, nanotubes, nanowires, molecular wires, molecular memories, molecular computers, molecular vehicles, molecular robots, nano-electronic/mechanical devices, etc.

Ⅲ. Research scope

In sharp contrast to conventional host-guest systems, the guests in our case include photons, electrons, and protons. We thus investigate the capabilities of manipulating individual photon, electron, proton, atom, ion, and molecule (for understanding the function in molecular devices/sensors) and the principles governing bio-molecular recognition, solvation mechanism, signal transduction, knowledge recognition, and memory retention in living systems. For practical utility, we design novel molecular electronic/photonic devices and molecular sensors.

Ⅳ. Achievements

Based on nanorecognition, self-assembly, and self-synthesis, we designed, synthesized, and characterized novel ionophores/receptors, functional organic nanotubes, coherently aligned metal sub-nanowires, and electrochemically controllable molecular nanodevices. We also predicted the left-handed helix (λ-helix) in proteins and the first nonlinear optical switches.

Ⅴ. Potential value of research

Knowledge of the governing forces in host-guest systems, molecular recognition, biomolecular structure and molecular assembly would be extremely useful in diverse fields of chemistry. Desinged inophores/receptors and nanotubes/nanowires would be useful for development of novel nanosensors and nanomaterials/nanodevices. Nanomechanical devices such as nano-vehicles would be useful for drug delivery and nanosurgery.

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(영 문 목 차)

목 차

제 1 장 연구개발과제의 개요

Chapter 1. Introduction: Research Objective

1. Problem Definition and Motive

During the last few years, the ideas envisioned in our original project proposal with theoretical design approach of nanomaterials and nanodevices have attracted the attention of several leading researchers in the world. Most of our visionary ideas have fructified into reality. There have been several efforts to develop single molecules as electronic components. Given the current interest in nanorecognition, the modulation of both structure and properties of matter upon interaction with electron/photon could be harnessed as chemosensors, nanodevices, or biochemical monitors. Since this kind of research requires ideas gleaned from both chemistry and physics, it is imperative that scientists from both these backgrounds should work on these problems, so as to fulfill our ultimate objective of the design and development of superfunctional materials.

Designing functional systems at the molecular level requires an intricate knowledge of the behavior of molecules. Furthermore, most of the traditional theoretical methods can no longer be employed to investigate these molecular level functional systems because of the emergence of quantum effects. Therefore, one has to employ high-level quantum mechanical methods, to analyze the structures, energetics, dynamics, and reactivity of existing systems, and to design new nano-scale materials and devices. Most of the existing theoretical methodologies have a lot of limitations as far as the characterization of these molecular level materials is concerned. Hence, new theoretical methodologies have to be developed from scratch. These methodologies require the effort of a number of scientists from different fields like physics, chemistry, and computer science. Once the molecular-level materials or devices have been designed, it is essential to synthesize and characterize some of them. Apart from enabling us to identify the flaws in the design process, it also helps to optimize the design strategy. The characterization of these materials requires the use of highly sophisticated experimental techniques, which include transmission electron microscopy, confocal microscopy, atomic force microscopy, scanning tunneling microscopy, etc. In the course of this research project, we intend to design and develop novel functional systems having widespread applications like nanoclusters, nanotubes, nanowires, molecular wires, molecular memories, molecular computers, molecular vehicles, molecular robots, nano-electronic/mechanical devices, etc. The research involved in designing and developing new functional systems would also have a number of spin-offs in many related areas, including (a) the elucidation of molecular recognition, (b) elucidation of molecular structure, reaction, and protein folding, and (c) understanding the principles underlying electron/proton transfer in molecules/materials and devices.

2. Research Scope

Our aim is an *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. We thus investigate the capabilities of manipulating an individual photon, electron, proton, atom, ion, and molecule (for understanding the function in molecular devices/sensors) and the principles governing bio-molecular recognition, solvation mechanism, 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 will be tested by synthesis and characterization of their properties. We include the study of electron/proton tunneling and current flow at molecular level. Based on these results, we design quantum molecular devices, and try to realize them. The key ideas of our goals are as follows:

(1) Designing novel superfunctional molecular systems through elucidation of host-guest interactions and molecular assemblies:

Host-guest molecular interactions play a key role in molecular recognition and in the design of novel molecular systems. However studies of such interactions have been extremely limited. We have been looking for unknown novel interactions. Using these results, we intend to design new types of host-guest molecular systems with superfunctional features. We have also studied interaction forces governing molecular assembly dynamics. Novel mimics of DNA, proteins, and enzymes can be designed using unusual assembly techniques. Topologically exotic supramolecular systems with special functions can be designed which would eventually lead to a new field in molecular assembly engineering. Our experience in designing novel self-assembled molecular systems would come in handy in this quest.

(2) Designing electron/photon/proton-host systems and studying its capture/release/transfer mechanisms and dynamics:

Electron transfer phenomena have an intrinsic quantum nature. This study is essential in understanding redox systems, biological signal transduction processes, and physical signal processes (such as in STM, AFM, and molecular electronic devices). We plan to design single electron electronic devices (such as diode/transistor for memory and CPU chips). This would herald in a new revolution in the information industry. In biology, this knowledge would help in understanding the intricacies of signal transduction processes and knowledge-recognition processes. Similarly, photon release/capture/transfer is closely related

to the electron transition. Thus, single photon manipulation process at the molecular level is also interesting. A related biological system of interest is bacteriorhodopsin in eye retina. An extension of this study would be useful in quantum optical information processing, quantum optical supersensor, and quantum mechanical photosynthesis. On the other hand, the proton transfer mechanisms of molecular systems associated with pH and pKa govern the solvation dynamics of biological important systems. We intend to extend the present limited understanding of these transfer mechanisms using a quantum dynamical approach by designing novel host-guest model systems, which mimic biological systems.

(3) Design and development of nanomaterials and nanodevices in finite dimensions and extreme conditions:

In low dimensions (1-, 2- dim), molecular species have completely different properties in contrast to those in 3-dimensions. Extreme conditions of temperature, pressure (including negative values) and external electromagnetic fields also change molecular properties. All these require a rigorous statistical and quantum mechanical approach. Above all, we plan to design nanomaterials to functiom as nanodevices. They include nanomechanical devices (nanovehicles, nanorobots), nanoelectronic devices (nanowires), nanosensors, and nanooptical devices (nanolenses).

As it can be seen, the diverse subjects discussed above have a common thread linking them i.e., the design of novel functional molecular systems based on the principles of quantum chemistry. A number of subtle phenomena which otherwise would be overlooked would emerge only after a systematic and detailed investigation is done using high levels of theory and computation in a methodical way. Such an investigation would help achieve our goals of the design and development of novel superfunctional-supermolecular systems.

This path-breaking research based on molecular quantum chemistry would open a new vista in science. Our optimism is based on our experience in designing functional molecules (which have actually been proved by experiments performed subsequent to our predictions) using this approach. Novel developments of practical molecular devices and sensors would herald a revolution in chemistry. The applications of this important field are stupendous with enormous impacts on information processing, life science, industry, medical technology, and human life. Most of the devices involve the electron, photon movements, or conformational changes. With our previously studied expertise on these systems, we can design novel functional materials and develop them to enhance their dynamical properties so as to be useful for molecular nanodevices.

제 2 장 국내외 기술개발 현황

Chapter 2. Background, Current Trend, and Future Direction

Our approach of a theoretical understanding of the problem preceding the actual experimental work is very unique and unlike those being pursued by other groups in the world. The successes we have achieved in the last couple of years, makes us optimistic that we would eventually succeed in our ultimate aim of *ab initio* design and development of novel superfunctional systems. In previous years, we had focused our attention on the elucidation of various intermolecular interaction forces and employed them in the design of a number of novel functional systems like ionophores, nanodevices, nanowires, etc. In the near future, we plan to continue our search for suitable hosts with guests like electrons, photons and protons. We believe that such a search would also aid us in the design of novel nanodevices and also help us understand the nature of the contact of nanowires with the electrodes. It is our belief that our search for superfunctional materials of practical utility would also be useful in understanding the principles governing molecular recognition, protein folding, signal transduction, memory retention, solvation, etc.

Our research center is ideally organized. Both theoretical/computational chemistry/physics design groups and experimental synthesis/characterization groups operate under the same roof with a common goal. Nearly all the scientists in the center have worked with renowned groups in their fields. Though many groups in the world work on molecular devices and functional molecules, almost all of them are only one of theoretical/computational chemistists/physicsists or experimental synthetic chemists/characterization physicists. Our center has been instrumental in breaking down the barriers between the traditional disciplines of physics, chemistry, biology, material science, and computer science. Thus, the center thrives on the communication between different groups and disciplines, which we believe is effective and essential in the design and development of new novel functional materials. The larger aims of the center include the *ab initio* design and development of novel functional molecular systems through an understanding of molecular functional mechanisms and assemblies. We will also plan to design novel molecular electronic/photonic devices and molecular sensors, which include single electron/photon devices and molecular tools to manipulate a single electron/photon. We intend to synthesize and characterize the most promising one of these predicted devices/sensors.

제 3 장 연구개발수행 내용 및 결과

Chapter 3. Results

1. Planned approaches for this research

In the course of the last few years, we have achieved some of the goals envisioned in our original project proposal. We therefore believe that our approach of a thorough understanding of the structural and electronic properties of the system, preceding their actual synthesis and characterization, is appropriate in meeting nearly all the goals envisioned in our original project proposal. While we would continue with our original idea of constructive collaboration of a number of chemists and physicists working on the project, we plan to further streamline our approach so that we could maintain our competitiveness and leadership in the research areas we are working on. Therefore, the plan of action for the next few years is as follows.

a) Design of novel superfunctional host-guest systems through elucidation of host-guest interactions and molecular assemblies:

In the last few years, we have designed and characterized several new ionophores, receptors, and chemosensors. Given the current demand for effective chemosensors, we plan to continue on our quest for more effective ionophores and receptors, so as to come up with practically useful systems. In particular, we are interested in developing suitable hosts for quantum guests like electrons, photons, and protons. Given the quantum nature of these species, it is imperative that we continue with our approach of using high-level quantum chemical calculations in conjunction with molecular dynamics and path-integral simulations to investigate the properties of these host-guest systems with and without the guests.

An area of related interest which has benefited from our theoretical investigations of the properties of functional systems is the identification of novel secondary structures of proteins. Given the current focus on bioinformatics and the interest in obtaining structure-function relationships of proteins, we believe that we should expend some efforts in that direction. In particular, we are interested in obtaining insights on prediction of secondary structures from amino-acid sequences.

b) *Investigation of the mechanisms of electron/photon/proton capture/release/transfer and their dynamics*:

While we have made significant breakthroughs in the elucidation of enzymatic reaction mechanisms, we still have to carry out a lot of work in understanding the mechanism of electron/photon/proton transfer in chemical and biological redox systems, signal transduction processes and molecular electronic devices. A step in that direction has been

taken in our investigations of the dynamics of an excess electron using molecular dynamics simulation. In order to take into account the quantum nature of these species more effectively, we intend to employ *ab initio* molecular dynamics simulations.

In a recent work, we had shown how the interaction of molecules with electrons/photons could be harnessed to make controllable nanodevices. In particular, we are interested in understanding the dynamics of molecules or molecular assemblies in their excited states. Such an understanding would aid us to design more efficient nanodevices. Our extensive work on the chemistry of molecular excited states would aid us in that quest.

Since the interaction of atoms or molecules with metal or molecular surfaces is found to be very useful in the manufacture of several electronic components, we believe that we should continue our pursuit of the interaction of various molecules with different surfaces. However, in our future studies, we also plan to take into consideration the interaction of excited state species of both atoms and molecules with surfaces.

c) *Design and development of nanomaterials and nanodevices in finite dimensions and extreme conditions*:

As was described earlier, we have made a significant breakthrough in the design and synthesis of ultrathin silver nanowires. However, our studies reveal that a major bottleneck in the practical utility of these ultrathin nanowires is their contacts with the electrodes. We intend to carry out detailed theoretical investigations of different contacts, so that we could come up with practical suggestions. While we have been successful in the synthesis of silver subnanowires, we also intend to investigate the possibility of synthesizing and characterizing other metallic and molecular subnanowires. Since there is relatively very little knowledge on how the properties (structural, mechanical, electrical, optical) of these nanowires are modulated as a result of a decrease in their lateral dimensions, we intend to carry out detailed theoretical investigations of the same.

2. Accomplishments and current status of research:

Based on an understanding novel intra-/inter-molecular interactions, we have been successful in designing novel functional materials and molecular devices. This novel research field is very original, quite different from what is being pursued anywhere else in the world. We have published 60 papers in highly reputed international journals (with the SCI citation impact number greater than ~3) and 3 book-chapters related to the proposal in the 2nd phase of the research. Despite this short period, these papers have been well cited (>600 times): Chem. Rev. (published in Nov. 00' 2nd phase, though submitted near the end of 1st phase) 130 times; Science (01') 90; J. Am. Chem. Soc (01'a) 40; J. Am. Chem. Soc (01'b) 25; J. Chem. Phys. (01') 25, etc. In particular, the work on nanotubes and encapsulated nanowires appeared on the *cover* of the Oct. 12, 2001 issue of "*Science*"

as well as *Science-Express*, and was highlighted in *Chem. & Eng. News* (C&E, Oct. 29, 2001). The discovery of a new left-handed λ-helix in protein was also highlighted in *Chem. & Eng. News* (C&E, Jan. 22, 2001). The number of cites to our earlier papers published in the 1st phase is also large: J. Chem. Phys. (98') 90; Proc. Natl. Acad. Sci. USA (98') 80; and a number of other papers > 50 times. We briefly summarize the accomplishments in the second phase (since Oct. 2000) in the below.

We have designed novel functional molecular systems through elucidation of molecular interactions, molecular assemblies, electron/photon/proton capture/release/transfer mechanism/ dynamics:

We have investigated various novel types of interaction forces responsible for diverse phenomena ranging from host-guest recognition and molecular assembly to chemical and enzymatic reactions have been characterized. In particular, their subtle differences have been elucidated, and applied for synthesis. Novel ionophores and receptors have been designed, synthesized, and characterized. These include belt-shaped and multi-podal molecular systems which selectively bind anions, cations, and organic ions including acetylcholine (which is related to Alzheimer desease), and amphi-ionophores in solution which are predicted to undergo dramatic structural changes upon binding either cations or anions. Assembly phenomena including formation of molecular clusters and metal-alloy nano-clusters as well as solvation phenomena have been elucidated.

Regarding protein structure, we first predicted the left-handed helix (λ-helix). We also elucidated the enzymatic role. The charge-dissipation/charge-buffering plays an important role to lower the activation barriers. This concept can be utilized to design novel enzymes.

The first nonlinear optical switch which can be controlled by laser was designed. This study is important in quantum optical information processing devices and sensors. A first electrochemically controllable molecular nanodevice was designed and synthesized as a precursor of electrochemically-controllable molecular vessel, which could be utilized as a means of drug delivery and nano-surgery.

We predicted physical properties of endohedral fullerenes, metal nanoclusters and nanowires. We designed, synthesized, and characterized functional organic nanotubes and coherently aligned metal sub-nanowires.

All these results would be utilized for better design/development of new nano-materials/devices.

A. Publications [Here we report 24 selected papers out of 60 papers on three main topics (A1-A3) carried out during the 2nd phase]

A1. Design of novel superfunctional molecular systems through elucidation of molecular interactions and assemblies:

(1a) Elucidation of the molecular interactions

During the last three years, we have consolidated our position as one of the world's leading groups involved in the elucidation of the intricacies of intermolecular interactions, by carrying out detailed theoretical investigations of π-H, cation-π, and π-rare gas interactions (*J. Am. Chem. Soc.* 123, 3323, 2001; *J. Chem. Phys*, 115, 6018, 2001; *J. Phys. Chem. A*, 107, 1228, 2003). We have also investigated the interaction of π-systems with several countermolecules like water clusters, rare gases, etc (*J. Chem. Phys.* 114, 1295, 2001; *J. Chem. Phys.* 114, 4016, 2001; *J. Chem. Phys.* 115, 10045, 2001; *J. Chem. Phys.* 117, 8805, 2002). As would be noted in subsequent sections, these investigations were of immense aid in the design of new functional materials.

[1] Title: Molecular Clusters of π-Systems: Theoretical Studies of Structures, Spectra, and Origin of Interaction Energies

Name of Journal (Publication Date): *Chem. Rev.* 100, 4145, (Nov. 2000)

Impact Factor of the Journal and Number of Citations: [20.99 106]

Authors: K. S. Kim,* P. Tarakeshwar, J. Y. Lee

Summary: This is a through investigation of interactions of various π-systems with diverse ligands ranging from the simplest rare-gas atom to the more complex water or methanol clusters. Some of salient results from theoretical calculations of these complexes, in particular, the effect of substituents of π systems and these interaction counterparts are discussed. It also points out that DFT method has some limitation in describing properly long-range dispersive interactions. This molecular interaction study has put a stepping stone for the design of nanomaterials.

[2] Title: Olefinic vs Aromatic π-H Interaction: A Theoretical Investigation of the Nature of Interaction of First-row Hydrides with Ethene and Benzene

Name of Journal (Publication Date): *J. Am. Chem. Soc.* 123, 3323 (2001).

Impact Factor of the Journal and Number of Citations: [6.20 31]

Authors: P. Tarakeshwar, H. S. Choi, K. S. Kim,*

Summary: The nature and origin of π-H interaction,which cannot be explain in such a conventional way as the electrostatic interaction, has been investigated. Various interaction energy components have been discussed based on the high level ab initio calculation results.

(1b) Ionophores/receptors

Our continuing quest in the design of novel ionophores and receptors has made several breakthroughs in the last couple of years. We identified a new class ionophores (amphi-ionophores), which exhibit high selectivity and affinity for both cations and anions even in aqueous solution (*J. Phys. Chem. B* 106, 2061, 2002). We designed, synthesized, and charcterizedseveral ionophores and receptors for biologically important anions like F-, Cl-, H2PO4- (*Org. Lett.* 4, 2897, 2002; *J. Org. Chem.* 68, 2467, 2003, *Org. Lett.* 5, 2083, 2003). The receptor for H2PO4- can also be employed as a chemosensor because ion binding leads to significant changes in the fluorescence of the receptor. Anion specific

receptors are extremely difficult to design and as a consequence several leading groups in the world have been involved in the endeavor. We have also designed several receptors for the biologically important molecule, acetylcholine (*Org. Lett.* 5, 471, 2003). Most previous attempts to design receptors specific for acetylcholine has been marred by the fact that these receptors also exhibit high selectivity and affinity for the ammonium cation. We have also identified a new family of carbon based ionophores, [n]-beltenes (*J. Org. Chem.* 67, 1848, 2002), wherein the ion-binding is mediated through the olefinic double bonds.

[3] Title: Tripodal Nitro-Imidazolium Receptor for Anion Binding Driven by (C-H)+---X- Hydrogen Bonds

Name of Journal (Publication Date): *Org. Lett.* 4, 2897, (July 19, 2002)

Impact Factor of the Journal and Number of Citation: [3.72 9]

Authors: H. Ihm, S. Yun, H. G. Kim, J. K. Kim, and K. S. Kim*

Summary: A positively charged tripodal receptor with nitro groups in the imidazolium rings was designed, synthesized, and characterized for its anion binding strength. The receptor shows strong affinity and high selectivity for Cl- through (C-H)+- - -X- hydrogen bonds wherein charge-charge and charge-dipole electrostatic interactions dominate. The association constant with chloride anion in a 9:1 mixture of acetonitrile-*d*3 and DMSO-*d*6 is measured to be 1.1 106 M-1. The receptor also shows reasonably high affinity toward H2PO4-.

[6] Title: Rational Design of Biologically Important Chemosensors: A Novel Receptor for Selective Recognition of Acetylcholine over Ammonium Cations

Name of Journal (Publication Date): *Org. Lett.* 5, 471, (January 28, 2003)

Impact Factor of the Journal and Number of Citation: [3.72 2]

Authors: S. Yun, Y. O. Kim, D. Kim, H. G. Kim, H. Ihm, J. K. Kim, C. W. Lee, W. J. Lee, J. Yoon, K. S. Oh, J. Yoon, S. M. Park, and K. S. Kim*

Summary: In consideration of competition between cation- and hydrogen bond interaction forces, we designed a novel receptor, 1,3,5-tris(pyrrolyl)benzene, which shows high selectivity for acetylcholine (ACh). The selectivity of the receptor for ACh over other ammonium cations is demonstrated by the ion-selective electrode (ISE) method in buffer solution. The binding free energy of the receptor with ACh in chloroform solution is measured to be 3.65 kcal/mol in the presence of chloride anion by nuclear magnetic resonance spectroscopy, and that in water is estimated to be much greater (~6 kcal/mol).This receptor is 25 times more selective for ACh than for NH4+, in contrast to other existing receptors which shows always higher selectivity for ACh.

(1c) Identification of a new folding motif in proteins (left-handed λ-helix)

One of the fundamental problems in chemistry, biology and medicine is an understanding of protein

folding. This understanding is extremely vital in the quest for new drugs against diseases like Alzheimer's, mad-cow, and other prion-based diseases. In this connection, our recent discovery of a hitherto unknown left-handed λ-helix merits mention (*J. Am. Chem. Soc.*123, 514, 2001). The importance of this work can be gauged by the fact that the work was highlighted in *Chem. & Eng. News* (*C&E,* p.52, January 22, 2001).

[9] Title: A New Type of Helix Pattern in Poly-Alanine Peptide

Name of Journal (Publication Date): *J. Am. Chem. Soc.* 123, 514, (January, 2001)

Impact Factor of the Journal and Number of Citation: [6.20 5]

Authors: H. S. Son, B. H. Hong, C. W. Lee, S. Yun, K. S. Kim*

Summary: In the presence of charged terminal ends, an unusual helical motif, a left-handed α-helix is found to be much more stable than a right-handed α-helix. This result could be useful for protein folding study, in particular, in the gas phase and in the nonpolar solvent environments, in considerationof the recent development in gas-phase experiments. The terminal end patching approach (using different charge conditions) could be utilized to control the handedness of protein folding as well as unfolding in nonpolar protein terminal segments.

A2. Investigation of the mechanisms of electron/photon/proton capture/release/transfer and their dynamics

(2a) Enzymatic reaction mechanisms

An understanding of the enzymatic reaction mechanisms is integral to our ultimate aim of an understanding of electron/photon/proton capture/release/transfer mechanisms and their dynamics. In work carried out in the earlier phase of this project, we had proposed the concept of short strong H-bond-induced partial proton shuttles and charge redistributions. In work carried out in this phase, we expanded our original proposal to a more generalized concept by including the charge-dissipation/buffering effect (*Biochemistry* 39, 13891, 2000; *J. Org. Chem.* 66, 6462, 2001 *J. Biol. Chem.* 277, 23414, 2002; *Biochemistry* 41, 5300, 2002). These investigations were carried out on *Ketosteroid Isomerases* and *Carboxypeptidase* enzyme. This work has potential applications in the development of new drugs.

[10] Title: Role of Catalytic Residues in Enzymatic Mechanisms of Homologous Ketosteroid Isomerases

Name of Journal (Publication Date): *Biochemistry* 39, 13891, (October 21, 2000)

Impact Factor of the Journal and Number of Citation: [4.06 13]

Authors: K. S. Oh, S. S. Cha, D. H. Kim, H. S. Cho, N. C. Ha, G. Choi, J. Y. Lee, P. Tarakeshwar, H. S. Son, K. Y. Choi,* B, -H. Oh,* and K. S. Kim*

Summary: Ketosteroid isomerase (KSI) is one of the most proficient enzymes catalyzing an allylic isomerization reaction at a diffusion-controlled rate. The structures of its active site and the role of various catalytic residueshave been reported. This investigation included the X-ray determination of 15 crystal structures of two homologous enzymes in free and complexed states (with inhibitors) and extensive ab initio calculations of the interactions between the active sites and the reaction intermediates. 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. The hydrogen bond distances in the intermediate analogues are found to be about 0.2 shorter in the product analogues both experimentally and theoretically.

[11] Title: Catalytic Mechanism of Enzymes: Preorganization, Short Strong Hydrogen Bond, and Charge Buffering

Name of Journal (Publication Date): *Biochemistry* 41, 5300, (January 7, 2002)

Impact Factor of the Journal and Number of Citation: [4.06 7]

Authors: K. S. Kim,* D. Kim, J. Y. Lee, P. Tarakeshwar, and K. S. Oh.

Summary: We clarified that thecatalytic mechanism needs to be explained with three important factors, viz., SSHB, preorganization, and charge buffering/dissipation. The charge buffering role of the catalytic residues is an important ingredient of the enzymatic reaction in reducing thelevel of accumulation of the negative charge on the substrate during the reaction process. This charge reduction is critical to the lowering of activation barriers and the stabilization of intermediates.

(2b) Dynamics of electrons and ions in aqueous solution

An understanding of the mechanism of electron transfer and dynamics in chemistry and biology is one of the original aims of this project. Towards this end, we investigated the dynamics of an excess electron in bulk water and the structures of small aqueous clusters containing either an halide anion or an excess electron (*J. Chem. Phys.* 114, 4461, 2001; *Mol. Phys.* 100, 875, 2002; *J. Chem. Phys.* 117, 706, 2002, *J. Chem. Phys.* 116, 5509, 2002; *J. Chem. Phys.* 118, 8681, 2003; *J. Chem. Phys.* 119, 187, 2003). The good agreement of the calculated and experimentally observed vibrational frequencies and vertical detachment energies indicate that most of our proposed structures are those being observed experimentally. This finding is of vital importance in our quest to design novel functional materials.

[12] Title: Structures and Spectra of Iodide-Water Clusters I-(H2O)n=1-6: *Ab Initio* Study

Name of Journal (Publication Date): *J. Chem. Phys.* 114, 4461, (March 8, 2001)

Impact Factor of the Journal and Number of Citation: [3.00 21]

Authors: H. M. Lee, and K. S. Kim*

Summary: To investigate the structures of I(H2O)*n* = 16, extensive *ab initio* calculations have been

carried out. Owing to very flexible potential surfaces of the system (in particular for $n = 5$ and 6), the lowest energy structures are characterized from various possible low-lying energy conformers. In contrast to some previously reported structures, we find a new lowest energy structure (followed by a few low-lying energy conformers) for $n = 5$ and four nearly isoenergetic conformers for $n = 6$. These conformers have surface and near-surface structures with the coordination number of 4. The present results provide the information of possible structures in recent profuse experiments of infrared spectra of I(H2O)n = 16 and charge transfer from the excited iodide ion to water molecules. Our predicted ionization potentials and OH stretching frequencies are in good agreement with the experimental data available, while only the cases of the OH frequencies for $n = 4$ and the ionization potential for $n = 5$ need consideration of conformational change by the temperature effect.

(2c) Interaction of photons/electrons with molecules: The quest to develop controllable nanodevices

The interaction of light with matter leads to several novel phenomena, which have potential applications in technology, telecommunication, medicine, etc. Most of these phenomena demand a detailed theoretical understanding of both the linear and nonlinear optical properties of molecules and materials. In particular, a detailed quantum-mechanical picture of how electrons move in these materials is essential for the quest of developing controllable nanodevices. Towards this end, we reported several new theoretical findings on the origin of nonlinear optical phenomena (*J. Chem. Phys.* 115, 9484, 2001; *J. Phys. Chem. A*, 107, 3577, 2003). We also investigated the isomerization of retinal chromophore and its derivatives (*J. Chem. Phys.* 116, 6549, 2002). This study on the interaction of electrons with important molecules was a forerunner to one of the highpoints of our work, which turned out to be the design and synthesis of an electrochemically controllable nanomechanical device as a precursor of molecular vessel which could be useful for drug-delivery and nanosurgery (*Org. Lett.*4, 3971, 2002). While the work described in this work was on a small molecular system, we believe that the work has potential applications in the design of more complex nanodevices.

[18] Title: An Electrochemically Controllable Nanomechanical Molecular System Utilizing Edge-to-face and Face-to-face Aromatic Interactions

Name of Journal (Publication Date): *Org. Lett.* 4, 3971 (October 9, 2002)

Impact Factor of the Journal and Number of Citation: [3.72 5]

Authors:H. G. Kim, C. W. Lee, S. Yun, B. H. Hong, Y. O. Kim, D. Kim, H. Ihm, J. W. Lee, E. C. Lee, P. Tarakeshwar, S. M. Park, and K. S. Kim*

Summary: A new molecular system, 2,11-dithio[4,4]metametaquinocyclophane containing a quinone moiety, was designed and synthesized. As the quinone moiety can readily be converted into an aromatic -system (hydroquinone) upon reduction, the nanomechanical molecular cyclophane system

exhibits a large flapping motion like a molecular flipper from the electrochemical redox process. The conformational changes upon reduction and oxidation are caused by changes of nonbonding interaction forces (devoid of bond formation/breaking) from the edge-to-face to face-to-face aromatic interactions and vice versa, respectively. This molecular flipper is an electrochemically controllable nanomechanical device as a precursor of molecular vessel which could be useful for drug-delivery and nanosurgery.

(2d) Mechanism of reactions on surfaces

The manufacture of several electronic components, to a large extent, depends on the interaction of small molecules with metal or molecular surfaces. In this connection, we have carried several theoretical investigations of the interaction of atoms (*Phys. Rev. B* 63, 073306, 2001; 63, 073066, 2001; 64, 235302, 2001; 65, 113306, 2002 *J. Phys. Chem. A* 106, 6817, 2002 106,9600, 2002). As would be seen in a subsequent section, these investigations are important in understanding the formation mechanisms of nanomaterials like nanotubes and nanowires.

A3. Studies of the properties of nanomaterials in finite dimensions and extreme conditions.

(3a) Encapsulated fullerenes

Continuing our quest to investigate the properties of materials in finite dimensions and extreme conductions, we investigated the nature of the interaction of highly reactive paramagnetic atoms like4N, 4P, 3O, 3S, with π sytems and endohedral fullerenes A@C60 (*J. Chem. Phys.*, 116, 10684, 2002). We also evaluated the energy barriers for penetration of the C60 cage by these paramagnetic atoms. The spin contained in the fullerene could be utilized as a qubit for the possible use of quantum computing system.

(3b) Organic nanotubes and silver nanowires

Using a novel design strategy, which coupled the advantages of H-bonding (the interaction is of intermediate strength and therefore reversible the interaction is directional and therefore one-, two-, three-dimensional structures can be readily assembled the assembly is often fast and specific) and weak π-πinteractions involving π-systems, we were successful in synthesizing and isolating organic calix[4]hydroquinone nanotube arrays with infinitely long one-dimensional H-bonds (*J. Am. Chem. Soc.* 123, 10748, 2001). Our work, which also involved detailed theoretical investigations, revealed that these nanotube arrays were formed from a subtle combination of both H-bonding and π-πinteractions. When calix[4]hydroquinone was reduced by silver nitrate, ultrathin single-crystalline subnaowire arrays were formed (*Science*, 294, 348, 2001 published as a *Sciemce-express*and put on the cover page of *Science*). The interesting aspect of these silver subnanowires was that they were

stable under ambient air and aqueous environments. This was unlike previously reported metal wires possessing ~1 nanometer diameters, which existed only transiently in ultrahigh vacuum. The silver subnanowires existed as coherently oriented three-dimensional arrays of ultrahigh density. Thus, they could be used as nanoconnectors for designing novel electronic components and nanoelectronic devices.We also carried out detailed theoretical investigations to understand the formation mechanisms and electronic properties of both the organic calix[4]hydroquinone nanotube (*J. Am. Chem. Soc.* 124, 14268, 2002) and the encapsulated silver subnanowire arrays (*Phys. Rev. B*(Rapid Commun.), 67, 241402 (R), 2003). Our calculations reveal that the conductance in these silver subnanowires is quantized. The work on both the organic nanotubes and silver nanowires was prominently highlighted in *Chem. & Eng. News* (*C&E,* p.22, October 22, 2001). In order to compare the properties of these silver subnanowires with other systems we carried out theoretical investigations of neutral silver and gold clusters (*J. Phys. Chem. A*, in press), pure silver, copper, and gold nanowires (Phys. Rev. B, 68, 033407, 2003), and the role of alloying on the properties of silver nanowires (Phys. Rev. B, 67, 233403, 2003)

[21] Title: Self-Assembled Organic Nanotube Arrays with Infinitely Long One-Dimensional H-Bonds

Name of Journal (Publication Date): *J. Am. Chem. Soc.* 123, 10748, (October 31, 2001)

Impact Factor of the Journal and Number of Citation: [6.20 20]

Authors: B. H. Hong, J. Y. Lee, C, -W. Lee, J. C. Kim. S. C. Bae, and K. S. Kim*

Summary: Organic nanotubes have been designed, synthesized, and characterized. In particular, a single organic nanotube was made. The nanotubes are used as templates for metal nanostructures by redox reaction.

[22] Title: Ultrathin Single-Crystalline Silver Nanowire Arrays Formed in an Ambient Solution Phase

Name of Journal (Publication Date): *Science* (September 6, 2001)

Impact Factor of the Journal and Number of Citation: [26.68 50]

Authors: B. H. Hong, S. C. Bae, C. W. Lee, S. Jeong, and K. S. Kim*

Summary: Single-crystalline silver nanowires of atomic dimensions are synthesized. The ultrathin silver wires with 0.4 width grow up to micrometer-scale length inside the pores of self-assembled calix[4]hydroquinone nanotubes by electro-/photochemical redox reaction in an ambient aqueous phase. The subnanowires are very stable under ambient air and aqueous environments, unlike previously reported metal wires of ~1 nanometer diameter, which existed only transiently in ultrahigh vacuum. The wires exist as coherently oriented three-dimensional arrays of ultrahigh density and thus could be used as model systems for investigating one-dimensional phenomena and as nanoconnectors for designing nanoelectronic devices.

[23] Title: Assembling Phenomena of calix[4]hydroquinone nanotube bundles by one-dimensional short hydrogen bonding and displaced π-π stacking

Name of Journal (Publication Date): *J. Am. Chem. Soc.* 124, 14268 (October 30, 2002)

Impact Factor of the Journal and Number of Citation: [6.20 6]

Authors: K. S. Kim,* S. B. Suh, J. C. Kim, B. H. Hong, E. C. Lee, S. Yun, P. Tarakeshwar, J. Y. Lee, Y. Kim, H. Ihm, H. G. Kim, J. W. Lee, J. K. Kim, H. M. Lee, D. Kim, C. Cui, S. J. Youn, H. Y. Chung, H. S. Choi, C. W. Lee, S. J. Cho, S. Jeong, and J. H. Cho

Summary: The assembly phenomena predicted prior to the synthesis of the nanotubes and details of the refined structure and electronic properties obtained after the experimental characterization of the nanotube crystal are reported. The competition between H-bonding and displaced π-πstacking in the assembling process has been clarified. The IR spectroscopic features and NMR chemical shifts of 1-D short H-bonds have been investigated.

[24] Title: Electronic Structure ofSilver Subnanowires in Self-Assembled Organic Nanotubes: Density Functional Calculations

Name of Journal (Publication Date): *Phys. Rev. B.* (Commun) 67, 241402, (June 13, 2003)

Impact Factor of the Journal and Number of Citation: [3.33 0]

Authors: S. B. Suh, B. H. Hong, P. Tarakeshwar, S. J. Youn, S. Jeong, and K. S. Kim*

Summary: First principles calculations have been coarried out to investigate the structure and electronic properties of ultrathin silver (Ag) nanowires self-synthesized in organic calix[4]hydroquinone (CHQ) nanotubes. The insulating CHQ nanotubes get transformed to semiconducting calix[4]diquinone-dihydroquinone tubes in the presence of Ag. These encapsulated nanowires have linear crystalline structure. The electron density around the Fermi level is localized on the Ag nanowire. This indicates that the organic tubes act as shields between Ag nanowires, and the quantum confinement is possible in the encapsulated Ag nanowires like in quantum dots.

B. Patents

[1] Title: Synthesis of organic nanotubes having suitable electrochemical and photochemical properties and synthesis of ultrathin nanowires using same as templates.

Application/Name of Country in which Registered (date):European Patent

Application/Person Registered: B. H. Hong, C. W. Lee, and K. S. Kim

Application/Registration Number: EP 1264919, December 2002

Patent Summary: Invention related to a method for synthesizing an organic nanotube and a method for synthesizing arrays of ultrafine nanowires using the organic nanotube as a template.

3. Representative Research Outputs

(1) Paper Title : Ultrathin Single-Crystalline Silver Nanowire Arrays Formed in an Ambient Solution Phase

○ Journal / Country, Year (Published) : Science / USA 294, 348 (2001. 10. 12)

○ Impact Factor of the Journal and Number of Citations: **[26.7;90]**

○ Authors : B. H. Hong, S. C. Bae, C. -W. Lee, S. Jeong, and K. S. Kim*

○ Summary : Single-crystalline silver nanowires of atomic dimensions are synthesized. The ultrathin silver wires with 0.4 nanometer width grow up to micrometer-scale length inside the pores of self-assembled calix[4]hydroquinone (CHQ) nanotubes by electro/photo-chemical redox reaction in an ambient aqueous phase. The subnanowires are stable under ambient air and aqueous environments, unlike previously reported metal wires of ~1 nanometer diameter, which existed only transiently in ultrahigh vacuum. The wires exist as coherently oriented three-dimensional arrays of ultrahigh density. These could be used as model systems for investigating one-dimensional phenomena and as nanoconnectors for designing nanoelectronic device.

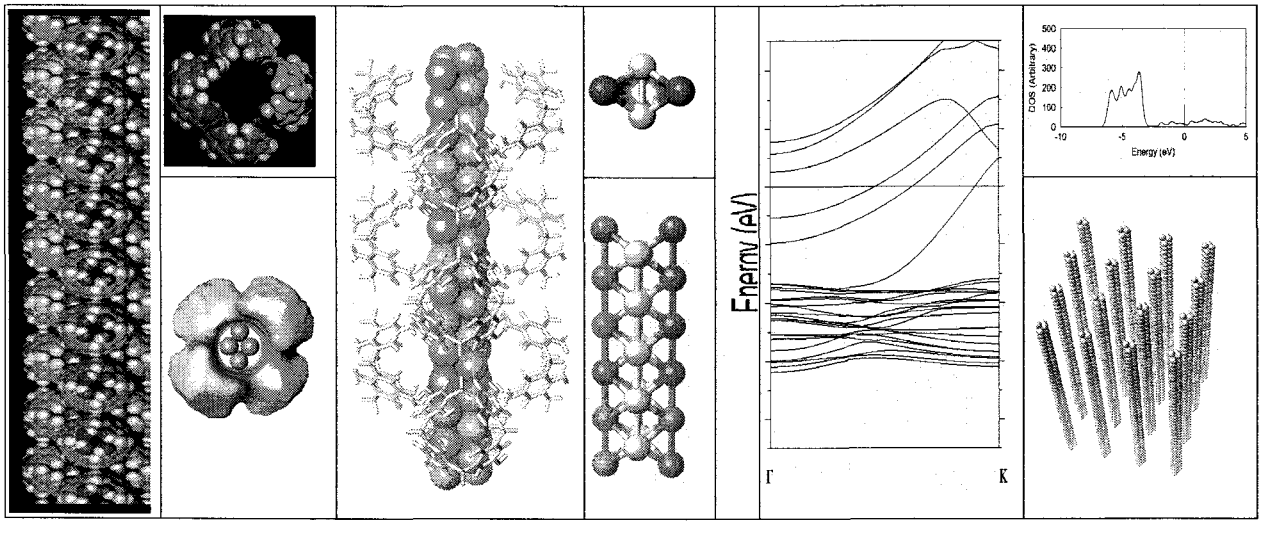


Figure: CHQ nanotube (left-most); encapsulated nanowire in nanotube (3rd left); bare silver nanowire (4th left); The calculated electronic structure (5th left) suggests that the silver nanowire is metallic. The s bands cross the Fermi level at three points, suggesting the existence of three conducting channels for electronic transport as a quantum wire. On the other hand, the calculation predicts that the CHQ nanotube is an insulator (with ~3 eV band gap) which shields the conduction between nanowires.; nanowire arrays (right-most). Originally published in Science Express as 10.1126/science.1062126 on September 6, 2001; Science, Vol. 294, Issue 5541, 348-351, October 12, 2001

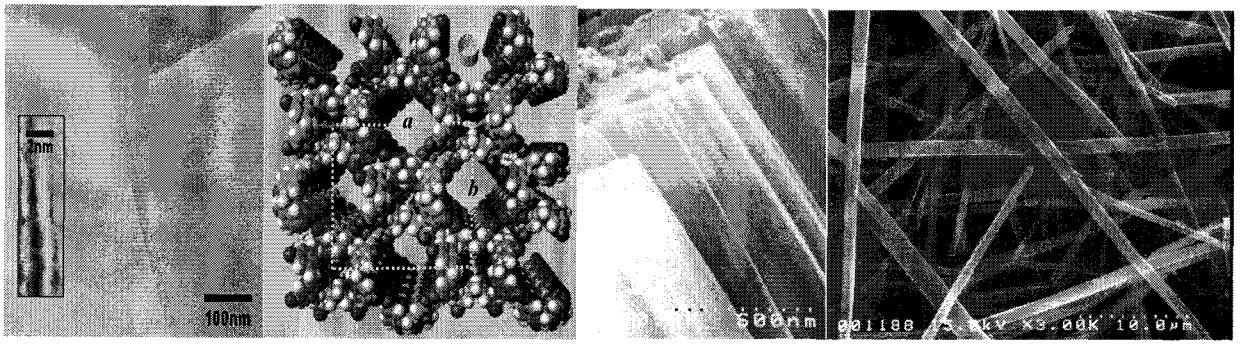
(2) Paper Title : Self-Assembled Organic Nanotube Arrays with Infinitely Long One-Dimensional H-bonds

○ Journal / Country, Year(Published) : J. Am. Chem. Soc. / USA
123, 10748 (2001. 10. 31)

○ Impact Factor of the Journal and Number of Citations: **[6.2; 25]**

○ Authors : B. H. Hong, J. Y. Lee, C.-W. Lee, J. C. Kim. S. C. Bae, and K. S. Kim*

○ Summary : Self-assembled organic nanotubes based on our theoretical background of intermolecular interactions (hydrogen bonding and aromatic-aromatic interactions) are designed, synthesized, and characterized. The self-assembled organic nanotube arrays composed of non-tubular sub-units of electrochemically and photochemically active calix[4]hydroqui-nones (CHQ). The crystal structure characterized by X-ray crystallography shows that the bundles of CHQ nanotubes form novel chessboard-like rectangular structures. Each nanotube has 17x17 $Å^2$ cross section with 6x6 $Å^2$ square pore (with the van der Waals volume excluded. The nanotubes have infinitely long one-dimensional (1D) H-bond arrays which have been observed for the first time. The 1D H-bond arrays help form a linear tubular polymer structure which can be suspended in aqueous solution, and also grown to very thin tubes as well as well-ordered arrays of tube bundles under aqueous environment. The strong reducing power of the nanotube is found to be of great use in designing nano-scale metal architecture. The nanotubes are used as templates for silver nanowires by redox reaction. The nanotubes arrays can be utilized in many interesting nanosystems. Utilizing the redox reaction of the nanotube with novel metal ions, we have made silver nanowire arrays, which would be useful for molecular electronic devices. The interesting structures and functions of CHQ nanotubes should find numerous applications, which are in progress in our laboratory.



(3) Paper Title : A New Type of Helix Pattern in Poly-Alanine Peptide

O Journal / Country, Year (Published) : J. Am. Chem. Soc. / USA.
123, 514, (2001, 1)

O Impact Factor of the Journal [6.2]

O Authors : H. S. Son, B. H. Hong, C. -W. Lee, S. Yun, and K. S. Kim*

O Summary : In the presence of charged terminal ends, an unusual helical motif, a left-handed lambda-helix is found to be much more stable than a right-handed alpha-helix. The results were based on quantum chemical calculations and molecular dynamic simulations. Since all previous helices were found to be right-handed, this left-handed helix is extremely surprising. This result could be useful for protein folding study, in particular, in the gas phase and in the nonpolar solvent environments, in consideration of the recent development in gas-phase experiments. The terminal end patching approach (using different charge conditions) could be utilized to control the handedness of protein folding as well as unfolding in nonpolar protein terminal segments. The understanding of the protein folding/unfolding problem is vital to the study of brain-related diseases (such as Alzheimer's disease and mad-cow disease).

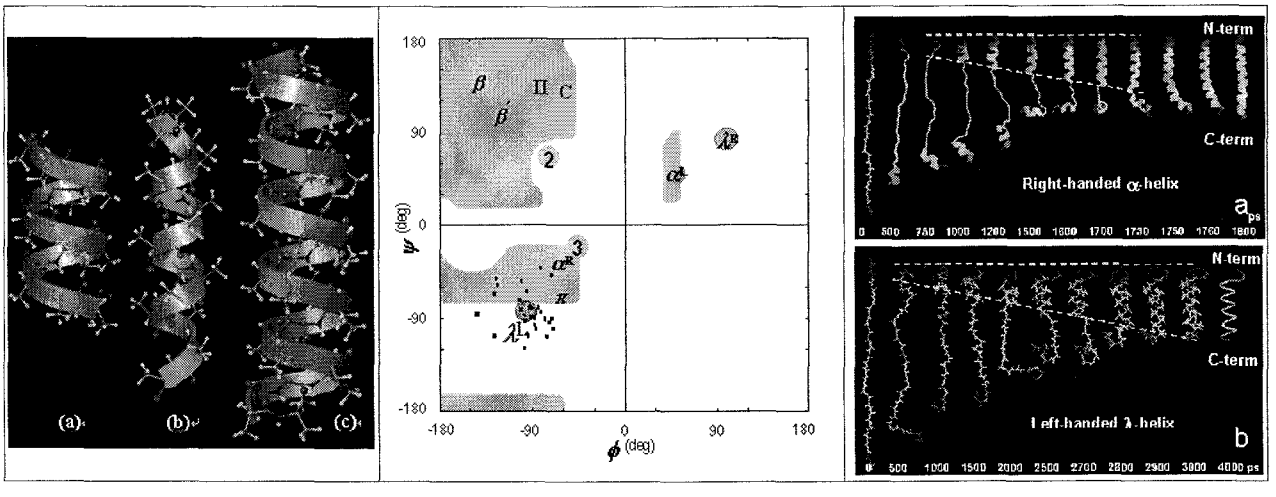


Figure (left): The idealized lambda helix pattern for NH_3^+-A_{15}-COO^- (**a**), the idealized lambda helix pattern for CH_3-A_{15}-NH_2 (**b**), and the lambda helix pattern from the NH_3^+-A_{30}-COO^- MD simulation (**c**). The idealized lambda and alpha helices have (φ,Ψ) angles of (-100°, -80°) and (-57°, -47°) respectively. **(middle):** Ramachandran plot for protein secondary structures composed of alanine amino acids. **(right):** Selected snapshots from MD trajectories. A right-handed alpha helix (a) and a left-handed lambda helix (b) are produced by the CH_3-A_{30}-NH_2 and the NH_3^+-A_{30}-COO^- simulations, respectively.

4. Self Appraisal

Based on an understanding novel intra-/inter-molecular interactions, we have been successful in designing novel functional materials and molecular devices. This novel research field is very original, quite different from what is being pursued anywhere else in the world. About 60 papers related to the proposal have been published in highly reputed international journals in the 2nd phase of the research (last 2 years). Most papers are well cited: Chem. Rev. (published in Nov. 00' 2nd phase; but work done during the end of 1st phase) > 100 times Science (01') >50 times; J. Am. Chem. Soc (01'a) > 30 times; J. Am. Chem. Soc (01'b) > 20 times; J. Chem. Phys. (01') > 20 times, etc. Given the number of cites of our earlier work, J. Chem. Phys. (98') > 80 times; Proc. Natl. Acad. Sci. USA (98') > 70 times and a number of other papers published in the 1st phase were cited over 50 times. In particular, the work on nanotubes and encapsulated nanowires appeared on the cover of the Oct. 12, 2001 issue of "Science" as well as Science-express, and was highlighted in Chem. & Eng. News (C&E, Oct. 29, 2001). The discovery of a new left-handed λ-helix in protein was also highlighted in Chem. & Eng. News (C&E, Jan. 22, 2001). Thel number of papers of the principal investigator is more than 180, and the total number of cites is about 3,000.

제 4 장 목표달성도

Chapter 4. Degree of Accomplishments toward the Original Goal

【Research objectives by phase】

Phase	Research objectives
Phase One	Elucidation of various interaction forces in molecular systems. Study of host-guest systems for molecular recognition. Study of functional molecular systems.
Phase Two	Molecular architecture based on interaction forces, assembly. Chemical/bio-functions (enzymes, protein enegineering, bioinformatics). Design of functional molecular systems. Synthesis and characterization of functional molecular systems.
Phase Three	Design of novel superfunctional molecular systems through elucidation of host-guest interactions and molecular assemblies. Investigation of mechanism of elctron/photon/proton capture/release/transfer and their dynamics. Properties of nanomaterials in finite dimensions and extreme conditions. Design of novel nanodevices/nanosensors.

【Phase Two: Research objectives by year】

Year	Research objectives	Research scope	Degree of Accomplishment
First year (2000-1)	Design of functional molecular systems Molecular architecture and aggregation	Assembly/aggregation, folding/unfolding, ionophores/receptors, functional molecular systems	100%
Second year (2001-2)	Theor/expt methodology develop Biofunctional mechanism Synthesis of functional molecules	Functional molecular systs., nanomaterials enzymes	100%
Third year (2002-3)	Characterization of functional molecular systems Preliminary design of molecular devices and sensors	nanomaterials characterization chemical/bio-sensors	100%

제 5 장 연구개발결과의 활용계획

Chapter 5. Potential Value of Research

1. Scientific and technological value

Significant advances have been made in recent years toward establishing the theoretical foundations and setting-up the experimental facilities needed for the design of functional materials and molecular devices/sensors. Since its inception, the center has been active on various fronts (intermolecular interactions, enzymatic reaction mechanisms, protein folding/unfolding, design of novel host-guest systems, nanotubes, nanowires, nanomechanical devices, etc.). Apart from the new methodology and ideas, which would be of extensive interest to the scientific community at large, the potential value of this research is given with the following examples:

eg.1. Knowledge of the governing forces in host-guest systems, molecular recognition, biomolecular structure and molecular assembly would be extremely useful in diverse fields of chemistry.

eg.2. Novel biofunctional molecules/mimics would be of extensive use in the pharmaceutical industry.

eg.3. Understanding of protein structure, function and mechanism of protein folding would be of interest to a large number of biologists.

eg.4. Some of the designed ionophores could be used to desalinate water and separate nuclear wastes.

eg.5. The designed single electron molecular electronic, photonic devices and nonlinear optical devices would be of use to the information industry.

eg.6. Knowledge of signal-transduction and knowledge-recognition processes would be of extensive interest to biologists and also help design efficient devices to transmit information.

eg.7. Understanding of the principles underlying photosynthetic processes would help create efficient mimics and devices capable of harnessing solar energy.

eg.8. Nanotubes/nanowires would be useful for development of nanomaterials and nanodevices.

eg.9 Nanomechanical devices such as nanovehicles would be useful for drug delivery and nanosurgery.

Most of these investigations are still in their embryonic stage. However the stage is being set to usher a new revolution in science. We believe that our stress on the development and continuation of some of the new ideas generated in the last six years are extremely vital to establish the center as a leading research institution in Korea and the world.

2. Further Research Plan

Our approach of a theoretical understanding of the problem preceding the actual experimental work is very unique and unlike those being pursued by other groups in the

world. The successes we have achieved in the last couple of years make us optimistic that we would eventually succeed in our ultimate aim of *ab initio*design and development of novel superfunctional systems. In previous years, we had focused our attention on the elucidation of various intermolecular interaction forces and employed them in the design of a number of novel functional systems like ionophores, nanodevices, nanowires, etc. In the near future, we plan to continue our search for suitable hosts for guests like electrons, photons and protons. We believe that such a search would also aid us in the design of novel nanodevices and also help us understand the nature of the contact of nanowires with the electrodes. It is our belief that our search for superfunctional materials of practical utility would also be useful in understanding the principles governing molecular recognition, protein folding, signal transduction, memory retention, solvation, etc.

In the course of the last few years, we have achieved some of the goals envisioned in our original project proposal. We therefore believe that our approach of a thorough understanding of the structural and electronic properties of the system, preceding their actual synthesis and characterization, is appropriate in meeting nearly all the goals envisioned in our original project proposal. While we would continue with our original idea of constructive collaboration of a number of physicists and chemists working on the project, we plan to further streamline our approach so that we could maintain our competitiveness and leadership in the research areas we are working on. Therefore, the plan of action, for the next few years is as follows.

a) Design of novel superfunctional host-guest systems through elucidation of host-guest interactions and molecular assemblies:

In the last few years, we have designed and characterized several new ionophores, receptors, and chemosensors. Given the current demand for effective chemosensors, we plan to continue on our quest for more effective ionophores and receptors, so as to come up with practically useful systems. In particular, we are interested in developingsuitable hosts for quantum guests like electrons, photons, and protons. Given the quantum nature of these species, it is imperative that we continue with our approach of using high-level quantum chemical calculations in conjunction with molecular dynamics, and path-integral simulations to investigate the properties of these host-guest systems with and without the guests.

An area of related interest which has benefited from our theoretical investigations of the properties of functional systems is the identification of novel secondary structures of proteins. Given the current focus on bioinformatics and the interest in obtaining structure-function relationships of proteins, we believe that we should expend some efforts in that direction. In particular, we are interested in obtaining insights on prediction of

secondary structures from amino-acid sequences.

b) *Investigation of the mechanism and dynamics of electron/photon/proton capture/release/transfer*:

While we have made significant breakthroughs in the elucidation of enzymatic reaction mechanisms, we still have to carry out a lot of work in understanding the mechanism of electron/photon/proton transfer in chemical and biological redox systems, signal transduction processes and molecular electronic devices. A step in that direction has been taken in our investigations of the dynamics of an excess electron using molecular dynamics simulation. In order to take into account the quantum nature of these species more effectively, we intend to employ *ab initio* molecular dynamics simulations.

In a recent work, we had shown how the interaction of a photon/electronwith molecules could be harnessed to make controllable nanodevices. In particular, we are interested in understanding the dynamics of molecules or molecular assemblies in their excited states. Such an understanding would aid us to design more efficient nanodevices. Our extensive work on the chemistry of molecular excited states would aid us in that quest.

Since the interaction of atoms or molecules with metal or molecular surfaces is found to be very useful in the manufacture of several electronic components, we believe that we should continue our pursuit of the interaction of various molecules with different surfaces. However, in our future studies, we also plan to take into consideration the interaction of excited state species of both atoms and molecules with surfaces.

c) *Studies of the properties of nanomaterials in finite dimensions and extreme conditions*:

As was described earlier, we havemade a significant breakthrough in the design and synthesis of ultrathin silver nanowires. However our studies reveal that a major bottleneck in the practical utility of these ultrathin nanowires is their contacts with the electrodes. We intend to carry out detailed theoretical investigations of different contacts, so that we could come up with practical suggestions. While we have been successful in the synthesis of silver subnanowires, we also intend to investigate the possibility of synthesizing and characterizing other metallic and molecular subnanowires. Since there is relatively very little knowledge on how the properties (structural, mechanical, electrical, optical) of these nanowires are modulated as a result of a decrease in their lateral dimensions, we intend to carry out detailed theoretical investigations of the same.

The ultimate aim of this project is to design superfunctional materials, which are of practical utility in biology, chemistry, medicine, physics, nuclear engineeringetc. Given the success of our approach of theory preceding the actual experimental synthesis and characterization, we are optimistic that we eventually would emerge with superfunctional materials of practical utility. One of the major spin-offs of our approach has been that we are able to obtain a theoretical understanding of hitherto unknown properties of even known systems.

특정연구개발사업 연구결과 활용계획서

<table>
<tr><td rowspan="2">사업명</td><td>중사업명</td><td colspan="4">특정연구개발사업</td></tr>
<tr><td>세부사업명</td><td colspan="4">창의적 연구 진흥 사업</td></tr>
<tr><td colspan="2">과제명</td><td colspan="4">초기능성 분자계의 설계와 개발 및 반응 기능기작과 분자조립 연구현상</td></tr>
<tr><td colspan="2">연구기관</td><td colspan="2">포항공과대학교</td><td>연구책임자</td><td>김광수</td></tr>
<tr><td colspan="2">총연구기간</td><td colspan="4">2000 년. 10 월. 1 일. ~ 2003 년. 9 월. 30 일. (36개월)</td></tr>
<tr><td colspan="2" rowspan="2">총 연구비
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표시)</td><td>1. 기업화 ( )</td><td>2. 기술이전( )</td><td>3. 후속연구추진( )</td><td>4.타사업에 활용( )</td></tr>
<tr><td>5. 선행 및 기초연구(x)</td><td>6. 기타목적활용(교육,연구)( )</td><td>7. 활용중단(미활용)( )</td><td>8. 기타( )</td></tr>
</table>

특정연구개발사업 처리규정 제 31조(연구개발결과의 보고) 제 2항에 의거 연구결과 활용계획서를 제출합니다.

첨부 : 1. 연구결과 활용계획서 1부.
2. 기술요약서 1부

2003 년 2 월 25 일

연구책임자 : 김 광 수 (인)

과학기술부장관 귀하

[첨부1]

연구결과 활용계획서

1. 연구목표 및 내용

The first aim is an *ab initio* design and development of novel functional molecular systems through our understanding of molecular functional mechanisms and assemblies. We have investigated capabilities of manipulating an individual photon/electron/proton/atom/molecule (for understanding the function in molecular devices/sensors) and the principles governing bio-molecular recognition (for developing novel drugs). The second aim, which is more practical utility, is to design novel molecular electronic/photonic devices and molecular sensors. Some of predicted devices/sensors will be tested by synthesis and characterization of their properties. We design and develop molecular devices. Therefore, the research aim can be outlined as (1) Designing novel functional molecular systems through elucidation of host-guest interactions and molecular assemblies, (2) Designing electron/photon/proton-host systems and studying its capture/release/transfer mechanisms, and (3) Physicochemical properties of nanomaterials in finite dimension as nanodevices.

2. 연구수행결과 현황(연구종료시점까지)

가. 특허(실용신안) 등 자료목록

[1] Title: Synthesis of organic nanotubes having suitable electrochemical and photochemical properties and synthesis of ultrathin nanowires using same as templates.

Application/Name of Country in which Registered (date):European Patent

Application/Person Registered: B. H. Hong, C. W. Lee, and K. S. Kim

Application/Registration Number: EP 1264919, December 2002

US Patent application No.: 10/075,486 (Aug 1, 2003).

Patent Summary: Invention related to a method for synthesizing an organic nanotube and a method for synthesizing arrays of ultrafine nanowires using the organic nanotube as a template.

나. 논문게재 및 발표 실적

ㅇ논문게재 실적(필요시 별지사용)

SCI Impact factor:3.0 이상만 기재:

A. Refereed Journals: 총 56 편

No.	*Title*	*Journal (Publ.Date)*	*Impact Factor (# Cited)*	*Authors*
1*	Ultrathin Single-crystalline Silver Nanowire Arrays Formed in an Ambient Solution Phase	Science 294, 348(2001)	26.68 (85)	B.H. Hong, S.C. Bae, C.-W. Lee, S. Jeong, K.S. Kim
2	Molecular Clusters of π-Systems: Theoretical Studies of Structures, Spectra and Origin of Interaction Energies	Chem. Rev. 100, 4145(2000)	20.99 (129)	K.S. Kim, P. Tarakeshwar, J.Y. Lee
3*	Self-Assembled Organic Nanotube Arrays with Infinitely Long One-Dimensional H-Bonds	J.Am.Chem.Soc. 123,10748(2001)	6.20 (32)	B.H.Hong, J.Y.Lee, C.-W.Lee, J.C.Kim, S.C.Bae, K.S. Kim
4*	A New Type of Helix Pattern in Poly-Alanine Peptide	J.Am.Chem.Soc. 123, 514(2001)	6.20 (6)	H.S. Son, B.H. Hong, C.-W. Lee, S. Yun, K.S. Kim
5	Assembling phenomena of calix[4]hydroquinone nanotube bundles by one-dimensional short hydrogen bonding and displaced π–π stacking	J.Am.Chem.Soc. 124, 14268 (2002).	6.20 (13)	K.S.Kim, S.B.Suh, J.C.Kim, B.H. Hong, E.C.Lee, S.Yun, P.Tarakeshwar, et. al.
6	Olefinic vs aromatic π-H interaction: A theoe-retical investigation of the nature of interaction of first-row hydrides with ethane/benzene	J.Am.Chem.Soc. 123, 3323 (2001)	6.20 (37)	P. Tarakeshwar, H.S. Choi, K.S. Kim
7	Trifluoroethanol increases the Stability of Δ^5-3-Ketosteorid isomerase from Pesudomonas testosteroni	J. Biol. Chem. 277, 23414 (2002)	6.70 (1)	S. Yun, D.S. Jang, G. Choi, K.S. Kim, K.Y.Choi, H.C.Lee.
8	Catalytic Mechanism of Enzymes: Preorganization, Short Strong Hydrogen Bond, and Charge Buffering	Biochemistry 41,5300 (2002)	4.06 (14)	K.S. Kim, D. Kim, J.Y. Lee, P. Tarakeshwar, K.S. Oh
9	Role of Catalytic Residues in Enzymatic Mechanisms of homologous Ketosteroid Isomerases	Biochemistry 39,13891 (2000)	4.06 (18)	K.S.Oh, S.-S.Cha, D.-H.Kim,H.-S.Cho, N.- C.Ha, G.Choi, J.Y.Lee, P.Tarakeshwar, H.S.Son, K.Y.Choi, B.-H.Oh,K.S.Kim
10	Tripodal Nitro-Imidazolium Receptor for Anion Binding Driven by $(C-H)^+$---X- Hydrogen Bonds	Org. Lett. 4, 2897 (2002)	3.72 (16)	H. Ihm, S. Yun, H.G. Kim, J.K. Kim, K.S. Kim
11	An Electrochemically Controllable Nano-mechanical Molecular System Utilizing Edge-to-face and Face-to-face Aromatic Interacions	Org. Lett. 4, 3971 (2002)	3.72 (8)	H.G. Kim, C.-W. Lee, S.Yun, B.H.Hong, Y.-O.Kim,D.Kim, H.Ihm,J.W.Lee, E.C.Lee, P.Tarakeshwar, S.-M.Park, K.S.Kim

12	A new fluoroscent photo-induced electron transfer chemosensor for the recognition of $H_2PO_4^-$	Org. Lett. 5, 2083 (2003)	3.72 (1)	S.K.Kim, N.J.Singh, S.J.Kim, H.G.Kim, J.K.Kim,J.W.Lee,K.S.Kim ,J.Yoon
13	Rational Design of Biologically Important Chemosensors: A Novel Receptor for Selective Recognition of Acetylcholine over Ammounium Cations	Org. Lett. 5, 471 (2003)	3.72 (4)	S. Yun, Y.-O. Kim, D. Kim, H.G.Kim, H. lhm, J.K. Kim, C.-W. Lee, W.J. Lee, J. Yoon, K. S. Oh, J. Yoon,S.-M. Park, K.S. Kim
14	Theoretical study of water adsorption on the Ge(100) surface.	Phys. Rev. B 65,113306(2002)	3.33 (2)	J. H. Cho, L. Kleinman, K.-J. Jin, K. S. Kim
15	Oscillatory energetics of flat Ag films on MgO(001)	Phys. Rev. B 63,113408(2001)	3.33 (4)	J.-H. Cho, K.S. Kim, C.T. Chan, Z. Zhang
16	Weakly correlated one-dimensional indium chains on Si(111)	Phys. Rev. B. 64,235302(2001)	3.33 (11)	J.-H. Cho, D.-H. Oh, K.S. Kim, K. Leonard
17	First-principles study of the adsorption of C2H2 on Si(100)	Phys. Rev. B 63,073306(2001)	3.33 (21)	J.-H. Cho, L. Kleinman, C.T. Chan, K.S. Kim
18	Electronic Structure of Silver Sub-nanowires in Self-Assembled Organic Nanotubes: Density Functional Calculations	Phys. Rev. B 67, 241402(R)(2003)	3.33 (1)	S.B.Suh, B.H.Hong, P.Tarakesh-war, S.J.Youn, S.Jeong, K.S.Kim
19	Large orbital magnetic moment and coulomb correlation effect in $FeBr_2$"	Phys. Rev. B 65,052415(2002)	3.33 (1)	S.J. Yoon, B.R. Sahu, K.S. Kim
20	Effect of dimensionality on the electronic structure of Cu, Ag, and Au	Phys. Rev. B 68,033407(2003)	3.33 (1)	T. Nautiyal, S. J. Youn, K. S. Kim
21	Linear monatomic wires stabilized by alloying: Ab initio density functional calculations	Phys. Rev. B 67,233403(2003)	3.33 (1)	W.-T. Geng, K.S. Kim
22	A New Type Ionophone Family utilizing the Cation-Olefine π Interaction: Theoretical Study of [n]Beltenes	J. Org. Chem. 67,1848(2002)	3.22 (5)	H.S. Choi, D. Kim, P. Tarakeshwar, S.B. Suh, K.S. Kim
23	Highly Stereospecific Epimerization of α-Amino Acids: Conducted Tour Mechanism	J. Org. Chem. 68, 6572 (2003)	3.22 (0)	I.Bandyopadhyay, H.M.Lee, C.Cui, P.Tarakeshwar, K.S.Oh, J.Chin, K.S.Kim
24	Molecular Recognition of Fluoride Anion: Benzene-Based Tripodal Imidazolium Receptor	J. Org. Chem. 68,2467(2003)	3.22 (7)	S. Yun, H. lhm, H.G. Kim, C.-W.Lee, B. Indrajit, K.S. Oh, Y.J. Gong, J.W. Lee, J. Yoon, H. C. Lee, K.S. Kim
25	Mechanistic Insight into the Inactivation of Carboxypeptidase	J. Org. Chem. 66,6462(2001)	3.22 (3)	S.J.Chung, S.Chung, H.S.Lee, E.-J.Kim, K.S.Oh, H.S.Choi, K.S.Kim, et al.

26	Anisole-(H2O)n (n=1-3) complexes: An experimental and theoretical investigation of the modulation of optimal structures, binding energies and vibrational spectra in both the ground/first excited states	J. Chem. Phys. 117, 8805 (2002)	3.00 (4)	B.Reimann, K.Buchhold, H.-D.Barth, B.Brutschy, P.Tarakeshwar, K.S.Kim
27	Structure, electronic properties, and vibrational spectra of the water octamer with an extra electron: Ab Initio Study	J. Chem. Phys. 117,706 (2002)	3.00 (14)	H.M. Lee, K.S. Kim
28	Water heptamer with an excess electron: Ab initio study	J. Chem. Phys. 118,9981(2003)	3.00 (5)	H. M. Lee, S.B. Suh, K. S. Kim
29	Structures, energetics and spectra of electron-water clusters, $e^-(H_2O)_6^-$ and e-HOD-$(D_2O)_5^-$	J. Chem. Phys. 119,187 (2003)	3.00 (7)	H.M. Lee, S. Lee, K.S. Kim
30	Structures and spectra of iodide-water clusters $I^-(H_2O)_{n=1-6}$: Ab initio study	J. Chem. Phys. 114,4461(2001)	3.00 (26)	H.M. Lee, K.S. Kim
31	Structures, spectra, and electronic properties of halide-water pentamers and hexamer, $X^-(H_2O)_{5-6}$ (X=F, Cl, Br, I): Ab initio study	J. Chem. Phys. 116,5509 (2002)	3.00 (20)	H.M. Lee, D. Kim, K.S. Kim
32	Ab initio study of the isomerization of retinal chromophore and its derivatives	J. Chem. Phys. 116,6549 (2002)	3.00 (4)	H.M. Lee, J. Kim, C.-J. Kim, K.S. Kim
33	Structures, energies, and vibration-al spectra of water undecamer and dodecamer: Ab initio study	J. Chem. Phys. 114,10749(2001)	3.00 (18)	H.M. Lee, S.B. Suh, K.S. Kim
34	Size scaling of intramolecular charge transfer driven optical properties of substituted polyenes and polyynes	J. Chem. Phys. (119, 7519 (2003)	3.00 (0)	J.Y. Lee, B.J. Mhin, S. Mukamel, K.S. Kim
35	Adsorption structure of 1,4-cyclohexadiene on Si(001)	J. Chem. Phys. 116, 3800(2002)	3.00 (3)	J.H. Cho, D.-W. Oh, K.S. Kim, L. Kleinman
36	Nature of the interaction of paramagnetic atoms (A=^{4}N, ^{4}P, ^{3}O, ^{3}S) with π systems and endohedral fullerenes A@C_{60}	J. Chem. Phys. 116,10684(2002)	3.00 (6)	J.M. Park, P. Tarakeshwar, K.S. Kim, T. Clark
37	Structure and stability of fluorine-substituted benzene-argon complexes: The decisive role of exchange-repulsion and dispersion interactions	J. Chem. Phys. 115, 6018(2001)	3.00 (10)	P. Tarakeshwar, K.S. Kim, E. Kraka, D. Cremer
38	Ab initio studies of π-water tetramer complexes: Evolution of optimal structures, binding energies and vibrational spectra of p-$(H_2O)_n$ (n=1-4) complexes	J. Chem. Phys. 114, 4016 (2001)	3.00 (9)	P. Tarakeshwar, H.S. Choi, K.S. Kim, S. Djafari, K. Buchhold, B. Reimann,H.-D.Barth, B.Brutschy
39	σ to π conformational transition: Interactions of the water trimer with π-systems	J. Chem. Phys. 114,1295(2001)	3.00 (14)	P. Tarakeshwar, K.S. Kim, B. Brutschy

40	Ab-initio studies of neutral and anionic p-Benzoquinone-water clusters	J. Chem. Phys. 118,8681(2003)	3.00 (4)	T. K. Manojkumar, H.S. Choi, P. Tarakeshwar, and K.S. Kim
41	Ab-initio studies of neutral and anionic Structures, energies, and spectra of aqua-silver(I) complexes	J. Chem. Phys. 119,7725(2003)	3.00 (0)	E.C. Lee, H. M. Lee, P. Tarakeshwar, K.S. Kim
42	Solvent rearangement For an excess electron of $I^-(H_2O)_6$: Analog to structural rearrangement of $e^-(H_2O)_6$	J. Chem. Phys. 119,7685(2003)	3.00 (0)	H.M. Lee, S.B. Suh, K.S. Kim
43	On the microscopic interaction of p-chlorofluorobenzene with water	J. Chem. Phys. 115,10045(2001)	3.00 (3)	C. Riehn, B. Reimann, K. Buchhold, H.-D. Barth, S. Vaupel, B. Brutschy, P.Tarakeshwar, and K.S. Kim
44	Intramolecular charge transfer of pi-conjugated push-pull systems in terms of polarizability and electronegativity	J. Chem. Phys. 115,9484(2001)	3.00 (6)	J.Y. Lee, K.S. Kim, B.J. Mhin
45	Theoretical Study of Microscopic Molecular Structure of Helicenebisquinone Aggregates	J.Phys.Chem.B 104,11006(2000)	3.61 (6)	H.S. Choi, K.S. Kim
46	Novel amphi-ionophone in aqulous solution: cyclohexaalaryl	J.Phys.Chem.B 106,2061(2002)	3.61 (5)	S.B. Suh, C. Cui, H.S. Son, J.S. Kim, U.Y. Won, K.S. Kim
47	Structural Stabilities and Self-Assembly of Cucurbit[n]uril (n=4-7) and Decamethylcucurbit[n]uril(n=4-6): A Theoretical Study	J.Phys.Chem.B 105,9726(2001)	3.61 (4)	K.S. Oh, J. Yoon, K.S. Kim
48	The molecular structure of para-cyclohexylaniline. Comparison of results obtained by X-lay diffraction with gasphase laser experiments and ab initio calculations	J.Phys.Chem.A 104,4016(2000)	2.77 (2)	C. Riehn, A. Degen, A.Weichert, M.Bolte, E. Egert, B. Brutschy, P. Tarakeshwar, K.S. Kim
49	Cation-Interactions: A Theoretical Investigation of the Interaction of Metalic and Organic Cations with Alenes, Arenes, and Heteroarenes	J.Phys.Chem.A 107,1128(2003)	2.77 (4)	D. Kim,S.Hu, P.Tarakeshwar, K.S. Kim, J. M. Lisy
50	New Quantum Chemical Parameter for the Substituent Effect in Benzene Based on Charge Flux	J.Phys.Chem.A 107,3577(2003)	2.77 (2)	J.Y. Lee, B.J. Mhin, K.S. Kim
51	Theoretical study of the gas phase Sc+(NO, O_2) ScO+(N, O) reactions	J.Phys.Chem.A 106,9600(2002)	2.77 (1)	K.H. Kim, Y.S. Lee, D. Kim, K.S. Kim, G.-H. Jeung
52	Insights into the Nature of SiH4-BH3 Complex: Theoretical Investigation of New Mechanistic Pathways Involving SiH3 and BH4 Radicals	J.Phys.Chem.A 106,6817(2002)	2.77 (6)	S. Hu, J, Kim, P. Tarakeshwar, K.S. Kim

53	Ring Opening Dynamics of a Photochromic Diarylethene Derivative in Solution	J.Phys.Chem.A 107, 8106(2003)	2.77 (0)	S. Shim, T. Joo, S. C. Bae, K.S. Kim, and E. Kim
54	Geometrical and Electronic Structures of Gold, Silver, and Gold-Silver Binary Clusters:Origins of Ductility of Gold and Gold-Silver Alloy Formation	J.Phys.Chem.A 107,9994(2003)	2.77 (0)	H.M. Lee, M. Ge, B.R. Sahu, P. Tarakeshwar, K.S. Kim
55	Structural, electronic, and magnetic properties of a ferromegnetic semiconductor: Co-doped TiO_2 rutile	Phys. Rev. B 68,125203(2003)	3.33 (1)	W.-T. Geng, K.S. Kim
56	Theoretical study of photoinduced electron transfer from tetramethylethylene to tetracyanoethylene	J. Chem. Phys. 119,8854(2003)	3.00 (0)	H.-B. Yi, X.-H. Duan, J.Y. Lee, H.M. Lee, X.-Y. Li, K.S. Kim

Total No. of Citations for the above 56 papers: 600

Total number of citations of the principal investigator's papers > 3,000.

B. Book Chapters Published:

(1) P. Tarakeshwar, D. Kim, H. M. Lee, S. B. Suh and K. S. Kim,*

"Theoretical Approaches to the Design of Functional Nanomaterials",

In "**Computational Material Science**", Edited by J. Leszczynski, Elsevier Publishers Amsterdam, 2003.

(2) P. Tarakeshwar and K.S. Kim,*

"Nanorecognition", In "**Encyclopedia of Nanoscience and Nanotechnology**",

Edited by H. S. Nalwa, American Science Publishers, California, 2003.

(3) P. Tarakeshwar, H. M. Lee, and K.S. Kim,*

"Insights from theoretical investigations of aqueous clusters",

In "**Reviews in Modern Quantum Chemistry** - A celebration of the contributions of R.G Parr",

Edited by K.D. Sen, World Scientific, Singapore, 2002, pp. 1642-1683.

○학술회의 발표 실적(필요시 별지사용): 계: 30건

Invited/Key-note/Plenary Talks and Organizing Chairs of International Conferences

(1) [invited talk] "Solvation phenomen: Lessons from Theoretical Investigations of Aqueous Clusters of Electrons, Ions, and pi Systems," Symp.on Solvated Molecules and Ions: Clusters to Condensed Phases,
PacifiChem 2000, Honolulu, Hawaii, USA (Dec. 14-19, 2000).

(2) [invited talk] "Self-assembled nanotubes and silver subnanowire arrays formed in and ambient solution phase", The First Korean-Swedish Bilateal Symposium, Seoul, Korea (Nov. 5-7, 2001).

(3) [invited talk; Organizing Chairman] "Catalytic role of enzymes: partial proton shuttles and charge redistributions",
The 9th Korea-Japan Joint Symposium, Okazaki, Japan (Jan. 10-12, 2001).

(4) [**plenary** talk] "De nove design of functional molecules, nanometerials, and nanodevices",
11th Current Trends for Computational Chemistry, Jackson State Univ. USA (Nov. 1-2, 2002).

(5) [**key-note** speaker] "De nove design of function nano-materials and molecular devices",
6th World Congress of Theoretically oriented Chemists, Lugano, Switzerland (Aug. 4-9, 2002).

(6) [invited talk] "Theoretical investigations of self-assembly in organic nanotubes",
223rd Am. Chem. Soc. (ACS) National Meeting, Orlando, FL, USA (April 7-11, 2002).

(7) [invited talk; Organizing Chairman] "Theoretical Insights into the kaleidoscopic world of gas phase clusters and nanomaterials",
10th Korea-Japan Joint Symposium on Theoretical/Computational Chemistry, Postech (Jan 12-15, 2003).

{The invited talks to be presented in the near future are as follows}

(8) {invited} "Theory , Modeling and Simulation", International Conference on Materials for Advanced Technologies (ICMAT 2003), Singapore, 2003 (Dec. 10-13, 2003).

(9) {invited} "Frontiers in Physical and Analytical Chemistry", 3rd Singapore International Chemical Conference, Singapore (Dec. 15-17, 2003).

(10) {invited; Organizing Chairman} "Theory and Application of Computational Chemistry", Gyeongju, Korea (Feb. 15-20, 2004).

(11) {invited} "Molecular Hosts for Anion Binding", 227th ACS Nat. Meeting, Anaheim, CA, USA (Mar.28-Apr.1, 2004).

(12) {invited} "Modeling and Simulating Materials Nanoworld", Sicily, Italy (May 30-June 4, 2004).
(13) {invited} "The Future of Force Field Modeling of Metal Complexes in the DFT Age", PacifiChem 2005, Honolulu, Hawaii, USA (Dec. 2005).
(14) {invited; Organizing Co-Chairman } "Computational Quantum Chemistry Methodology and Application",
PacifiChem 2005, Honolulu, Hawaii, USA (Dec. 2005).
(15) {invited; Organizing Chairman} "Design of Nanomaterials and Nanodevices",
PacifiChem 2005, Honolulu, Hawaii, USA (Dec. 2005).

*** Invited talks at many foreign universities and national laboratories ***:
(1) "July-Aug. 2002": Max Plank Inst. (Mainz) Univ. Frankfurt Univ. Bonn; Acad. of Sci. Czech Republic.
(2) "Oct. 2002": Univ. Illinois (Urbana-Champaign); Northwestern Univ.; Georgia Inst. Tech.; Univ. of Colorado, (Boulder); Pacific Northwest National Lab.
(3) "March 2003": Univ. Texas (Austin); Georgia Inst. Tech. (Phys); Univ. Pittsburgh; Yale Univ.

3. 기술이전 및 연구결과 활용계획

In the course of the last few years, we have achieved some of the goals envisioned in our original project proposal. We therefore believe that our approach of a thorough understanding of the structural and electronic properties of the system, preceding their actual synthesis and characterization, is appropriate in meeting nearly all the goals envisioned in our original project proposal. While we would continue with our original idea of constructive collaboration of a number of chemists and physicists working on the project, we plan to further streamline our approach so that we could maintain our competitiveness and leadership in the research areas we are working on. Therefore, the plan of action for the next few years is as follows.

a) Design of novel superfunctional host-guest systems through elucidation of host-guest interactions and molecular assemblies:
In the last few years, we have designed and characterized several new ionophores, receptors, and chemosensors. Given the current demand for effective chemosensors, we plan to continue on our quest for more effective ionophores and receptors, so as to come up with practically useful systems. In particular, we are interested in developing suitable hosts for quantum guests like electrons, photons, and protons. Given the quantum nature of these species, it is imperative that we continue with our approach of using high-level quantum

chemical calculations in conjunction with molecular dynamics and path-integral simulations to investigate the properties of these host-guest systems with and without the guests.
An area of related interest which has benefited from our theoretical investigations of the properties of functional systems is the identification of novel secondary structures of proteins. Given the current focus on bioinformatics and the interest in obtaining structure-function relationships of proteins, we believe that we should expend some efforts in that direction. In particular, we are interested in obtaining insights on prediction of secondary structures from amino-acid sequences.

b) *Investigation of the mechanisms of electron/photon/proton capture/release/transfer and their dynamics*:
While we have made significant breakthroughs in the elucidation of enzymatic reaction mechanisms, we still have to carry out a lot of work in understanding the mechanism of electron/photon/proton transfer in chemical and biological redox systems, signal transduction processes and molecular electronic devices. A step in that direction has been taken in our investigations of the dynamics of an excess electron using molecular dynamics simulation. In order to take into account the quantum nature of these species more effectively, we intend to employ *ab initio* molecular dynamics simulations.
In a recent work, we had shown how the interaction of molecules with electrons/photons could be harnessed to make controllable nanodevices. In particular, we are interested in understanding the dynamics of molecules or molecular assemblies in their excited states. Such an understanding would aid us to design more efficient nanodevices. Our extensive work on the chemistry of molecular excited states would aid us in that quest.
Since the interaction of atoms or molecules with metal or molecular surfaces is found to be very useful in the manufacture of several electronic components, we believe that we should continue our pursuit of the interaction of various molecules with different surfaces. However, in our future studies, we also plan to take into consideration the interaction of excited state species of both atoms and molecules with surfaces.

c) *Design and development of nanomaterials and nanodevices in finite dimensions and extreme conditions*:
As was described earlier, we have made a significant breakthrough in the design and synthesis of ultrathin silver nanowires. However, our studies reveal that a major bottleneck in the practical utility of these ultrathin nanowires is their contacts with the electrodes. We intend to carry out detailed theoretical investigations of different contacts, so that we could come up with practical suggestions. While we have been successful in the synthesis of silver subnanowires, we also intend to investigate the possibility of synthesizing and

characterizing other metallic and molecular subnanowires. Since there is relatively very little knowledge on how the properties (structural, mechanical, electrical, optical) of these nanowires are modulated as a result of a decrease in their lateral dimensions, we intend to carry out detailed theoretical investigations of the same.

4. 기대효과

a) Scientific and technological value:

Significant advances have been made in recent years toward establishing the theoretical foundations and setting-up the experimental facilities needed for the design of functional materials and molecular devices/sensors. Since its inception, the center has been active on various fronts (intermolecular interactions, enzymatic reaction mechanisms, protein folding/unfolding, design of novel host-guest systems, nanotubes, nanowires, nanomechanical devices, etc.). Apart from the new methodology and ideas, which would be of extensive interest to the scientific community at large, the potential value of this research is given with the following examples:

eg.1. Knowledge of the governing forces in host-guest systems, molecular recognition, biomolecular structure and molecular assembly would be extremely useful in diverse fields of chemistry.

eg.2. Novel biofunctional molecules/mimics would be of extensive use in the pharmaceutical industry.

eg.3. Understanding of protein structure, function and mechanism of protein folding would be of interest to a large number of biologists.

eg.4. Some of the designed ionophores could be used to desalinate water and separate nuclear wastes.

eg.5. The designed single electron molecular electronic, photonic devices and nonlinear optical devices would be of use to the information industry.

eg.6. Knowledge of signal-transduction and knowledge-recognition processes would be of extensive interest to biologists and also help design efficient devices to transmit information.

eg.7. Understanding of the principles underlying photosynthetic processes would help create efficient mimics and devices capable of harnessing solar energy.

eg.8. Nanotubes/nanowires would be useful for development of novel nanomaterials and nanodevices.

eg.9 Nanomechanical devices such as nanovehicles would be useful for drug delivery and nanosurgery.

Most of these investigations are still in their embryonic stage. However the stage is being set to usher a new revolution in science. We believe that our stress on the development and continuation of some of the new ideas generated in the last six years are extremely vital to establish the center as a leading research institution in Korea and the world.

b) Social and economical value:

Hightech nanosystems would be very important for improving the standard of life. Since the nanoelectronic devices would revolutionize the information technology and the nanomechanical devices would be very useful for nanosurgery and drug deliverly system, the development of novel nanoelectronic devices and nanomechanical devices would be of great value for future economy as well as human life. The applications of this important field are stupendous with enormous impacts on information processing, life science, industry, medical technology, etc.

[첨부2]

기술 요약서

■ 기술의 명칭

신기술: 유기 나노관 및 금속 나노선의 합성

■ 기술을 도출한 과제현황

과제관리번호	M10018000020			
과제명	초기능성 분자계의 설계와 개발 및 반응 기능기작과 분자조립 연구현상			
사업명	특정 연구 개발 사업			
세부사업명	창의적 연구 진흥 사업			
연구기관	포항공과대학교		기관유형	
참여기관(기업)				
총연구기간	6 년			
총연구비	정부(20,500)천원 민간( )천원 합계(20,500)천원			
연구책임자 1	성명	김광수	주민번호	500206-1067925
	근무기관 부서	포항공대 화학과	E-mail	kim@postech.ac.kr
	직위/직급	교수	전화번호	054-279-2110
연구책임자 2	성명		주민번호	
	근무기관 부서		E-mail	
	직위/직급		전화번호	
실무연락책임자	성명		소속/부서	
	직위/직급		E-mail	
	전화번호		FAX	
	주소	(-)		

■ 기술의 주요내용

[기술의 개요]

본 발명은 유기 나노관(organic nanotube)의 합성 및 이 유기 나노관을 주형으로서 이용하여 산화-환원 반응을 통해 이온 상태의 금속으로부터 초미세 금속 나노선(ultrathin nanowire)을 합성하는 방법에 관한 것으로, 본 발명에 따르면 기존의 합성법과는 달리 상온, 상압의 용액 상에서 합성이 수행되므로 매우 실용적으로 유기 나노관 및 금속 나노선을 얻을 수 있을 뿐만 아니라, 수득된 유기 나노선은 극히 작은 지름을 가지므로 고집적회로 및 기억 소자의 개발에 유용하게 이용될 수 있다.

<기술적 특징>

(1)기존의 합성법과는 달리, 상온, 상압의 용액상에서 모든 실험이 이루어지므로 매우 실용적이다.

(2)지금까지 학계에 보고된 나노선 중 가장 작은 지름의 특성을 가질 뿐 아니라 일정한 공간적 배열을 이루고 있어 현 기술의 수천 배 이상의 집적도를 가진 회로 및 기억소자 개발에 획기적인 기여를 할 것으로 기대된다.

(3)

[용도 · 이용분야]

본 발명에 따른 CHQ 나노관은 자기-정렬성 유기 나노관으로서, 수성 환경 하에서 매우 얇을 뿐 아니라 관 다발의 잘 정렬된 배열체로 성장될 수 있다. 본 발명에 따른 유기 나노관은 양성자/전자 터널링 현상 및 기타 물리적, 화학적 특성면에서 우수하다.

본 발명의 나노관의 강한 환원력을 이용하여 나노관을 주형으로 이용함으로써 금속 이온의 나노 구조체를 용이하게 제조할 수 있다.

■ 기술의 분류

[기술코드] □□□ (3 Digit) (KISTEP 홈페이지 기술요약서용 기술분류표 참조)

[기술분야] (1개만 선택(∨로 표시)하여 주십시오)

□ 정보산업 □ 기계설비 □ 소재 ☑ 정밀화학 · 공정 □ 생명과학
□ 원자력 □ 자원 □ 에너지 □ 항공 · 우주 □ 해양
□ 교통 □ 보건 · 의료 □ 환경 □ 기초 · 원천 □ 기타

[기술의 활용유형] (1개만 선택(∨로 표시)하여 주십시오)

□ 신제품개발 ☑ 신공정개발 □ 기존제품개선 □ 기존공정개선
□ 기 타 ( )

[기술의 용도] (복수 선택(∨로 표시)가능합니다)

□ 기계설비 □ 부품소자 □ 원료재료 □ 소프트웨어
□ 가공처리기술 □ 자동화기술 □ 불량률 감소 등 현장애로기술
□ 제품설계기술 □ 공정설계기술 □ 기 타 ( )

■ 산업재산권 보유현황(기술과 관련한)

권리유형	명 칭	국가명	출원단계	일자	등록번호

* '권리유형'란에는 특허, 실용신안, 의장, 컴퓨터프로그램, 노하우 등을 선택하여 기재
* '출원단계'란에는 출원, 공개, 등록 등을 선택하여 기재

■ 기술이전 조건

이전형태	□ 유상 □무상	최저기술료	천원
이전방식	□ 소유권이전 □ 전용실시권 □ 통상실시권 □ 협의결정 □ 기타( )		
이전 소요기간	년 개월	실용화예상시기	년도
기술이전시 선행요건			

* 기술이전시 선행요건 : 기술이전을 위한 사전준비사항(필수 설비 및 장비, 전문가 확보 등)을 기술
* 실용화예상시기 : 기술을 활용한 대표적인 제품이 최초로 생산이 시작되는 시기를 기재

■ 기술의 개발단계 및 수준

[기술의 완성도] (1개만 선택(∨로 표시)하여 주십시오)

	① **기초, 탐색연구단계** : 특정용도를 위해 필요한 신 지식을 얻거나 기술적 가능성을 탐색하는 단계
	② **응용연구단계** : 기술적 가능성의 실증, 잠재적 실용화 가능성의 입증 등 실험실적 확인 단계
	③ **개발연구단계** : Prototype의 제작, Pilot Plant Test 등을 행하는 단계
	④ **기업화 준비단계** : 기업화에 필요한 양산화 기술 및 주변 기술까지도 확보하는 단계
	⑤ **상품화 완료단계**

[기술의 수명주기] (1개만 선택(∨로 표시)하여 주십시오)

	① **기술개념 정립기** : 기술의 잠재적 가능성만 있는 단계
	② **기술실험기** : 기술개발에 성공했으나 아직 실용성, 경제성 등이 확실치 않은 단계
	③ **기술적용 시작기**: 최초의 기술개발국에서만 활용되고 있는 단계
	④ **기술적용 성장기**: 기술개발국 및 일부 선진국에서 활용되고 있는단계
	⑤ **기술적용 성숙기**: 선진국사이에서 활발한 기술이전이 일어나며, 기술의 표준화가 되어가는 단계
	⑥ **기술적용 쇠퇴기**: 선진국에서 개도국으로 기술이전이 활발하게 일어나고, 선진국에서는 기술의 가치가 저하되나, 개도국에서는 아직 시장의 가치가 높은 기술

[기술발전 과정상의 기술수준] (1개만 선택(∨로 표시)하여 주십시오)

	① **외국기술의 모방단계** : 이미 외국에서 개발된 기술의 복제, reverse Eng.
	② **외국기술의 소화·흡수단계** : 국내시장구조나 특성에 적합하게 적응시킴
	③ **외국기술의 개선·개량단계** : 성능이나 기능을 개선시킴
	④ **신기술의 혁신·발명단계** : 국내 최초로 개발

■ 본 기술과 관련하여 추가로 확보되었거나 개발중인 기술

[기술개요]

기술명	
개발단계	☐ 연구개발 계획 ☐ 연구개발 중 ☐ 연구개발 완료
기술개요	

[기술을 도출한 과제현황]

과제관리번호				
과제명				
사업명				
세부사업명				
연구기관			기관유형	
참여기관(기업)				
총연구기간				
총연구비	합계 : ( )백만원 - 정부 : ( )백만원 민간 : ( )백만원			
연구책임자	소속		성명	
	전화번호		E-mail	
연구개발 주요내용				

주 의

1. 이 보고서는 과학기술부에서 시행한 특정연구개발사업의 연구보고서입니다.
2. 이 보고서 내용을 발표할 때에는 반드시 과학기술부에서 시행한 특정연구개발사업의 연구결과임을 밝혀야 합니다.
3. 국가과학기술 기밀유지에 필요한 내용은 대외적으로 발표 또는 공개하여서는 아니됩니다.