

## De novo design approach based on nanorecognition toward development of functional molecules/materials and nanosensors/nanodevices\*

N. Jiten Singh, Han Myoung Lee, Seung Bum Suh, and Kwang S. Kim<sup>‡</sup>

*Department of Chemistry, Center for Superfunctional Materials, Pohang University of Science and Technology, Pohang, 790-784, Korea*

**Abstract:** For the design of functional molecules and nanodevices, it is very useful to utilize nanorecognition (which is governed mainly by interaction forces such as hydrogen bonding, ionic interaction,  $\pi$ -H/ $\pi$ - $\pi$  interactions, and metallic interactions) and nanodynamics (involving capture, transport, and release of electrons, photons, or protons). The manifestation of these interaction forces has led us to the design and realization of diverse ionophores/receptors, organic nanotubes, nanowires, molecular mechanical devices, molecular switches, enzyme mimetics, protein folding/unfolding, etc. In this review, we begin with a brief discussion of the interaction forces, followed by some of our representative applications. We discuss ionophores with chemo-sensing capability for biologically important cations and anions and explain how the understanding of hydrogen bonding and  $\pi$ -interactions has led to the design of self-assembled nanotubes from calix[4]hydroquinone (CHQ). The binding study of neutral and cationic transition metals with the redox system of hydroquinone (HQ) and quinone (Q) predicts what kind of nanostructures would form. Finally, we look into the conformational changes between stacked and edge-to-face conformers in  $\pi$ -benzoquinone-benzene complexes controlled by alternating electrochemical potential. The resulting flapping motion illustrates a promising pathway toward the design of mobile nanomechanical devices.

**Keywords:** nanorecognition; computer-aided molecular design; functional molecules; functional materials; nanosensors; nanodevices.

### INTRODUCTION

Molecular-level functional materials and devices are of great importance because of possible applications in the fields of information storage, communication and computation, and material and biological sciences. Much of our recent success in de novo design of materials [1] is attributed to the understanding of the nanorecognition phenomena [2] of molecules and materials involving self-assembly and self-engineering. This understanding helps us investigate chemical and physical properties of novel nanomaterials. Of course, experimental synthesis and measurements based on intuition and experiences have made many important contributions in designing functional molecules and nanomaterials over the past

\*Paper based on a presentation at the 18<sup>th</sup> International Conference on Physical Organic Chemistry (ICPOC-18), 20–25 August 2006, Warsaw, Poland. Other presentations are published in this issue, pp. 955–1151.

<sup>‡</sup>Corresponding author: E-mail: kim@postech.ac.kr

years. However, as the systems become smaller and smaller, the quantum nature of molecules and materials is important, and so the exploitation of the commonsense alone has been limited in designing novel nanosystems. It is necessary to create a new paradigm for the design approach, because the systems involved in quantum phenomena are hardly comprehensible by intuition and simple experiences. Theoretical methods have been instrumental in their ability to help understand the variation of chemical and physical properties as single atoms or molecules coalesce to form larger functional entities [3–9]. In this regard, computational methods, apart from providing unique insights into experimental data, have guided experimentalists toward the design of new materials with unique and important properties [4]. For practical utility, functional materials need to be self-assembled, and nanodevices would be self-engineered. To this end, the nanorecognition should play an important role. The chemical and physical properties of most nanomaterials are a manifestation of several types of interatomic, intramolecular, and intermolecular interactions, which can be either cooperative or competitive. A judicious combination of various types of intermolecular interactions would lead to self-assembly process of given molecular systems including self-synthesis, which would result in ideal molecular engineering process toward smart self-engineered functional molecular systems and nanomaterials.

In the course of this review, we examine how an effective combination of diverse theoretical methods has helped elucidate the nature of intermolecular interactions in a number of selected examples. At the onset, we will discuss briefly the different types of interaction forces whose relevance is of importance to the *de novo* design of nanosensors, nanomaterials, and nanodevices. Thus, the manifestation of these intermolecular forces is the computer-aided design of novel nanomaterials such as ionophores/receptors, endo/exohedral fullerenes, fullerides, nanotori, nanotubes, nanowires, and molecular devices. Here we discuss some of the representative examples of the applications manifested based on the principles of nanorecognition.

## INTERMOLECULAR INTERACTIONS

### Computational methods

The nature of the intermolecular interactions in dimeric complexes or larger clusters can be ascertained by using a judicious combination of supermolecular (SM) variational and perturbational methods [8]. The former method is employed to carry out geometry optimizations and evaluate vibrational frequencies. Presently, SM calculations are broadly based on Hartree–Fock theory, density functional theory (DFT), and a high level of *ab initio* theory such as Møller–Plesset (MP) perturbation, configuration interaction (CI), complete active-space self-consistent field (CASSCF), coupled-cluster singles and doubles (CCSD), etc. Since the inclusion of electron correlation is vital to obtain an accurate description of most of the calculated properties, most of the SM calculations were carried out at either the second-order Møller–Plesset perturbation (MP2) or the coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)] using basis sets composed of polarization and diffuse functions.

Even though the SM method is conceptually and computationally simple, it does not provide a clear picture of the interaction forces responsible for the interaction. On the other hand, the perturbation method enables one to obtain a physical picture of the interactions prevailing between monomers involving complexation. This is because of the fact that in the SM method, the interaction energy is evaluated as the difference of the energy of the complex and the energy of the isolated monomers. However, in the perturbational method, the interaction energy is obtained as a sum of individual electrostatic, exchange, dispersion, and induction energies [10].

As the size of the system increases, it is impossible to carry out calculations at the levels of theory employed in the investigation of the smaller systems. Therefore, DFT methods have been widely employed in a large number of studies because of the smaller computational resources needed to describe very large systems. In particular, they have been found to be effective in the description of sys-

tems dominated by hydrogen-bonding interactions, but their use in the description of weak intermolecular complexes is limited by the inability of most current functionals to describe dispersion energies. In these cases, the calculations based on MP2 and CCSD(T) are required.

### Types of intermolecular interactions

In order to have a theoretical understanding of the so-called nanorecognition, we need to have a detailed understanding of various types of intermolecular interactions. Though a large number of intermolecular interactions prevail in chemical and biological systems, it could be broadly classified into five different types: (i) hydrogen bonding, (ii) ionic interactions, (iii) intermolecular interactions involving  $\pi$ -systems, (iv) metallic interactions, and (v) interactions involving quantum species. The physical properties of most nanomaterials are a manifestation of several of these intermolecular interactions, which can be either cooperative or competitive. As a result, the magnitude of each intermolecular interaction in the nanomaterial of interest is either enhanced or depleted. Thus, judicious combination of these interaction forces would be essential for the design of smart self-engineered functional molecular systems and nanomaterials. Detailed discussion of these interaction forces is not possible within the scope of this overview; however, we provide the main essence of these interaction forces based on our theoretical investigations in the past years. Though metallic interaction is also an important force associated with regard to nanorecognition, we do not consider this interaction force within the scope of this overview. However, the details could be found elsewhere [11–13].

### Hydrogen bonding

Hydrogen bond (H-bond) is the most vital interaction force both in biology and chemistry [14–18]. For instance, water (which is the most abundant and essential substance on our planet) and proteins and DNA (which are the most important substances in biosystems) are held basically by networks of H-bonds. The H-bond energy ranges from 2 to 20 kcal/mol, while the most typical H-bond energy is ~5 kcal/mol in zero-point energy uncorrected binding energy and ~3 kcal/mol in zero-point energy corrected dissociation energy [19]. Since H-bonds can be easily formed and broken depending on the given environment, they are considered to have “on or off” functions in biology. Hydrogen bonding also finds relevance in nanomaterial design because (i) the interaction is of intermediate strength and therefore reversible; (ii) the interaction is directional and therefore one-, two-, three- dimensional structures can readily be assembled by hydrogen bonding; and (iii) the assembly is often fast and specific.

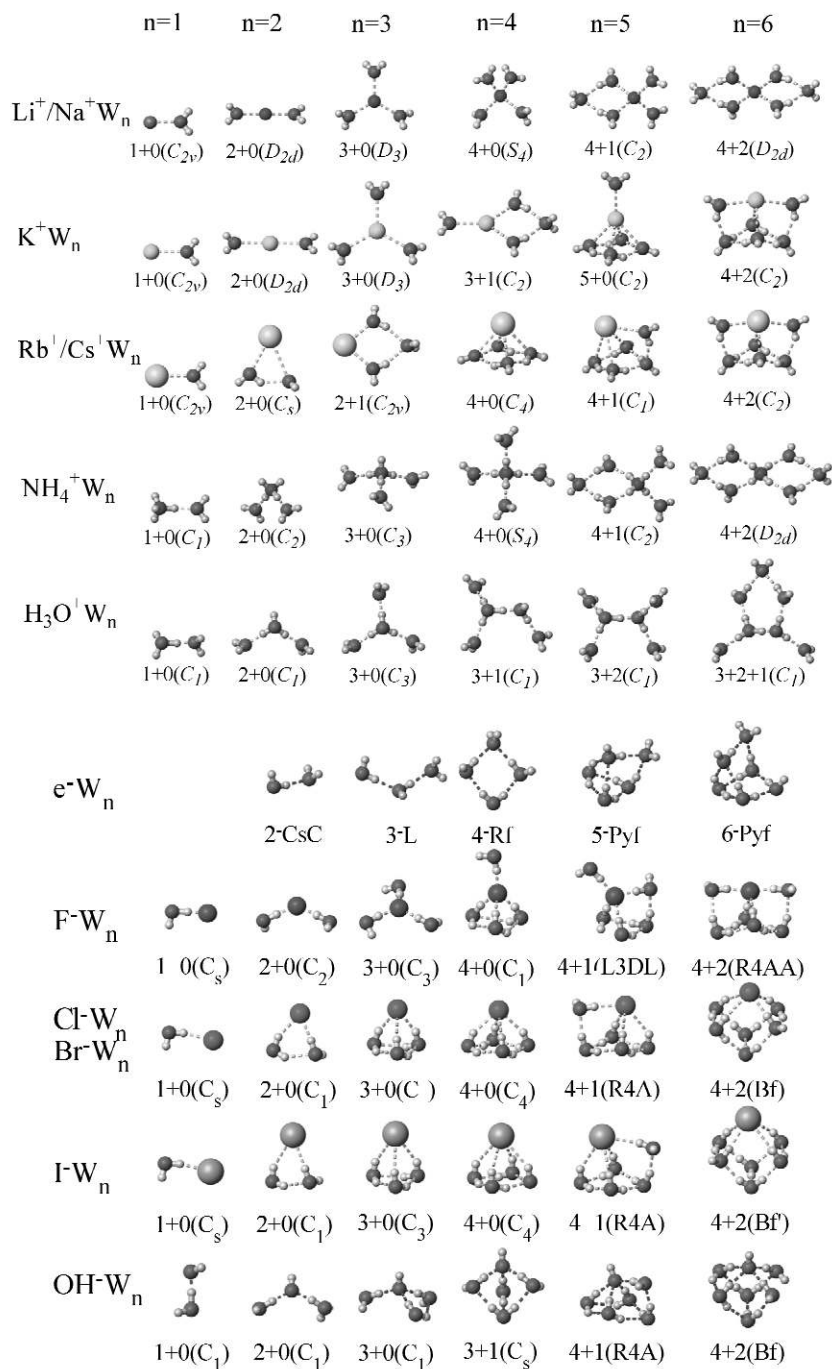
In general, hydrogen bonding is characterized by a dominant contribution from electrostatic energies. However, as the attractive electrostatic contribution is to a large extent cancelled by the repulsive exchange energy, the sum of induction and dispersion energies is nearly equivalent to the total interaction energy. When a system possesses multiple H-bonds, cooperativity is a particularly characteristic manifestation, which has important consequences in nanomaterial design. For example, in water clusters, the average energy of a H-bond progressively increases with an increase in the cluster size [20,21]. This enhancement of interaction energies leads to a progressive decrease in the intermolecular H-bond distance, and, hence, significant geometry changes can also be noted.

In addition, we should mention special types of H-bonds such as ionic H-bonds [22], positively charged H-bonds [23,24], negatively charged H-bonds [25,26], short H-bonds [27], short strong H-bonds [28–33], and aromatic H-bonds ( $\pi$ -H interactions) [34–44].

### Ionic interactions

Since electrostatic energies dominate intermolecular interactions between cations and anions involving ionic species, these interactions are specially considered as ionic interactions. Since this cation–anion

interaction is almost ubiquitous, and easy to understand, the details of this well-known interaction are not discussed here. Nevertheless, a significant difference is noted in the solvation of cationic and anionic species as a result of the fact that these intermolecular interactions binding the ions to the solvent are dominated by electrostatic and inductive energies. Electrostatic interactions involving anions are less effective because they have a lower ratio of charge to radius than isoelectronic cations, while the polarization effect in anions becomes significant. In particular, the non-valence-type excess electron around the anion (except for  $F^-$ , which has partially valence-like excess electron) needs a large empty space to be stabilized simply due to the uncertainty principle [45]. Thus, the anion needs an empty space on one side, while it interacts with ligands on the other side (Fig. 1). Furthermore, while cations prefer to interact with heavy non-hydrogen atoms (such as oxygen and nitrogen) [46–49], anions interact with the smaller-sized hydrogen atoms [50–55]. As a consequence, the electron clouds of the anion are anisotropically and directionally polarized toward the electron acceptor sites (in most cases, H-atoms). Full coordination is therefore difficult to achieve in the case of anion solvation, as the columbic repulsion between H-atoms of solvents or ligands prevents them to come too close to each other. In general, the geometries and interaction energies of cationic-water clusters are nearly independent of the level of theory at which the calculations are carried out. Of course, the calculations involving the large alkali cations [56,57] as well as organic and heavy metal cations [58–60] yield more accurate results when electron correlation is explicitly included. In sharp contrast, calculations on anion-containing systems should explicitly include electron correlation. This inclusion of electron correlation becomes more important in intermolecular interactions involving  $\pi$ -systems, because these interactions are mediated through the more diffuse  $\pi$ -electron cloud. The ionic interaction is useful in the fields ranging from nanoclusters to the guest–host complexes [61–63].



**Fig. 1** Structures of the  $\text{M} \cdot (\text{H}_2\text{O})_{1-6}$ , ( $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+, \text{H}_3\text{O}^+$  as cationic species and  $\text{M} = \text{e}^-$ ,  $\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-$  as anionic species) complexes.

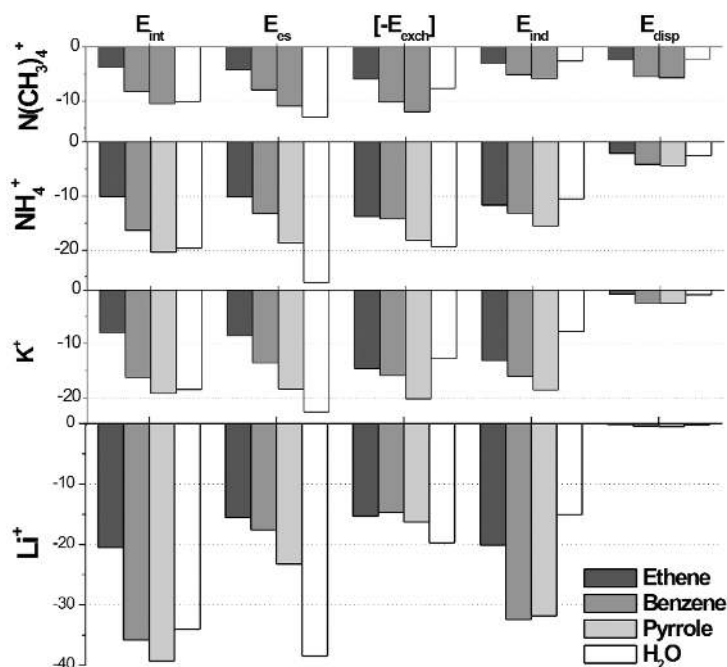
### Intermolecular interactions involving $\pi$ -systems

Interactions involving  $\pi$ -systems are most relevant in the context of nanomaterial design [1,64–67]. These interactions are perceptibly weak to be observed experimentally, and their accurate description requires very high levels of theory [8,68–85]. A large number of nanosystems ranging from fullerenes to ionophores exhibit these interactions, hence it is important to theoretically investigate the nature of these interactions. Interactions involving  $\pi$ -systems can be utilized in the fabrication of nanodevices, because subtle changes in the electronic characteristics of the  $\pi$ -systems can lead to dramatic effects in the structure and properties of the nanosystem [86,87].

A broad classification of the nature of the interactions involving these  $\pi$ -systems can be based on the nature of the countermolecule involved in the interaction. A combination of electrostatic and induction energies dominate the interaction when the countermolecule is a metal cation. For the interaction of a positively charged organic cation with the negatively charged  $\pi$ -electron cloud, an accurate estimate of the interaction energies requires the inclusion of other factors like the polarizability of the  $\pi$ -system. The importance of dispersion energies in the binding of the tetramethyl ammonium and ammonium cation to benzene is well demonstrated [88–90]. Dispersion energies predominate when the countermolecule is either a rare gas atom or a nonpolar molecule (gas dimers, hydrocarbons) [91]. When the countermolecule is either a polar molecule or Lewis acid, both electrostatic and dispersion energies govern the interaction [92,93]. The magnitude of the repulsive energies plays a vital role in governing the observed geometry of clusters containing  $\pi$ -systems [90]. It can be noted here that the magnitudes of the electrostatic and induction energies in the case of the organic cation complexes of these  $\pi$ -systems are much smaller than those observed in the case of the  $\pi$ -alkali metal cation complexes, while the contribution of dispersion energies becomes vital.

While comparing the cation–water interactions with cation– $\pi$  interactions [90,94–111], the distinction between them is the magnitude of the electrostatic energies, which are dominant contributors to the total interaction energy in the case of the former [90] (Fig. 2). In the context of nanomaterial design, these findings are significant because a greater electrostatic contribution implies that the magnitudes of the interaction energies are more susceptible to the dielectric of the environment. Nearly similar interaction energies of the benzene with the ammonium and potassium cations result from a balance of dispersion and induction energies because the electrostatic and exchange energies are nearly similar and hence mostly cancel out. However, the ammonium cation complexes exhibit a larger contribution of dispersion energies [88–90]. In a subsequent section, we show how suitable receptors specific for the ammonium cation could be designed by enhancing the contribution of the dispersion energies. In the context of the cation– $\pi$  interactions, it is interesting to note that many anion receptors are found to have augmented anion binding affinity due to the presence of aromatic ring moieties which interact with the anions (anion– $\pi$  interactions [112–117]) in addition to other binding arms. Even though the total interaction energies of anion– $\pi$  complexes are comparable to those of the corresponding cation– $\pi$  complexes, the largest contributions to the total interaction energy in the former complexes are the electrostatic and the induction energies. However, in contrast to the cation– $\pi$  interaction, the contribution from the dispersion energies is substantial, and in complexes involving organic anions, their magnitudes are comparable to electrostatic and induction energies. Apart from increases in both the induction and dispersion energies, the anion– $\pi$  interactions are also characterized by a substantial increase in the magnitude of the exchange-repulsion energy.

Complexes exhibiting the  $\pi$ –H interaction are of interest because this interaction is also a hydrogen bond. In going from  $\text{CH}_4$  to  $\text{NH}_3$ , to  $\text{H}_2\text{O}$ , to  $\text{HF}$ , the increase in the repulsive exchange energies is more pronounced in the ethene than in the benzene complexes [78]. This leads to a smaller variation in the intermolecular distances in the benzene complexes. Consequently, the magnitude of the dispersion energies is nearly independent of the nature of the hydride, because the magnitude of the dispersion energies is nearly proportional to the number of electrons participating in the interaction and the inter-



**Fig. 2** Comparison of cation– $\pi$  and cation–water interactions. Notice the distinct differences in various interaction energy components as a result of changes in the nature of the cation and the  $\pi$ -system. Reproduced by permission of American Chemical Society [90].

molecular distance. We also note an increase in the magnitude of the induction energies of the hydride complexes of both ethene and benzene upon inclusion of electron correlation.

The  $\pi$ – $\pi$  interactions are one of the most intriguing noncovalent interactions, in the sense that the negatively charged and diffuse electron clouds of the  $\pi$ -systems exhibit an attractive interaction. This interaction is predominated by dispersion interactions, when the  $\pi$ -systems possess nearly similar electron densities. However, when one of the systems is electron-rich (benzene) and the other electron-deficient (hexafluorobenzene), the resulting complexes are bound by induction interactions with the negative charge being transferred from benzene to hexafluorobenzene [118,119]. The acetylene dimer is one of the simplest systems exhibiting a  $\pi$ – $\pi$  interaction [120,121]. Though a parallel displaced conformer involving a stacking of the two acetylene  $\pi$ -systems exhibit a  $\pi$ – $\pi$  interaction, the most stable conformer is a T-shaped structure, which involves the interaction of hydrogen of acetylene with the  $\pi$ -system of the other. In the case of the ethene dimer, the most stable structure has a  $D_{2d}$  symmetry, which involves the formation of a quadruple hydrogen bond [122]. The interaction of two benzene rings (benzene dimer) has been widely investigated both experimentally and theoretically. The experimental estimates of the interaction energy is of the order of  $\sim 2$  kcal/mol [123,124], which indicates that the attraction is appreciable and significantly influences the interaction of phenyl rings in solution or other environments, in addition to other factors such as solvophobic effects. The interaction is predominated by dispersion interactions [77,78–82]. As in the case of the acetylene dimer, the benzene dimer can manifest itself in T-shaped or parallel-displaced conformers. The available evidence seems to indicate that the edge-to-face conformer is the most stable, but nearly isoenergetic to parallel displaced conformation. The isolated benzene dimer is extremely floppy and can coexist in both forms. On the other hand, while considering the facial or axial substitution effect on the edge-to-face aromatic interaction, we observed that for the axially substituted aromatic systems, the electron density at the para position is an important stabilizing factor, and thus the stabilization/destabilization by substitution of an aro-

matic ring is governed mostly by the electrostatic energy [77]. In a while, the dispersion energy is mostly canceled out by the exchange repulsion. Thus, the stabilization/destabilization by substitution is governed mainly by electrostatic energies. On the other hand, the facially substituted aromatic system depends on not only the electron-donating ability responsible for the electrostatic energy, but also the dispersion interaction and exchange repulsion. The dispersion energy, together with the exchange repulsion, augments the electrostatic energy in the facially substituted aromatic systems. In a subsequent section, we take advantage of the fact that the interconversion between different conformers or the orientations of the two interacting  $\pi$ -systems can be exquisitely controlled [86]. In order to have maximum control on this interconversion, we use the electrochemically and photochemically active  $\pi$ -systems (Q and HQ) [87].

### Interactions involving quantum species

While most of the previous discussion on intermolecular interactions was involved in molecules, atoms, or stable closed-shell cations or anions, the interactions involving quantum species like single electrons [125–129], protons [49,90], photons [130–132], and paramagnetic atoms [133] have been found to be of importance in understanding the modulation of properties by external stimuli. These stimuli could be from the photochemical (involving photons) [130–132] and chemical (involving changes in ion and pH concentrations) [86] to electrical (involving electrons) [13,129,134] and spintronic [12,133] origins. Most of the current work on intermolecular interactions involving quantum species has implications in nanomaterial design because it paves the way to several desirable goals like responsive and intelligent materials, smart sensors, molecular devices, etc. It should, however, be mentioned that the theoretical methods which can be used to tackle these problems are still in their infancy.

### Cooperative and competing interactions

Since a vast majority of intermolecular interactions are weak, they are reversible. However, molecules possessing multiple complementary binding sites provide a means to magnify the effect of very weak individual interactions. This effect is more commonly known as cooperativity and is responsible for the physical characteristics of a vast majority of chemical and biological systems. In most cases, the entropic effects need not be invoked to explain this phenomenon in nanoscale systems, due to their small contributions at low and non-high temperatures. In general, the existence of multiple binding sites in natural or synthetic receptors leads to greater efficiency and selectivity in complexation. What is interesting about cooperativity is that conformational changes occurring during the course of complexation can be harnessed for the design of functionally important systems.

One of the widely known manifestations of cooperative effects which is of relevance to our discussion is self-assembly. A number of studies on hydrogen bonding in organic molecular assemblies have revealed that certain classes of functional groups always form H-bonds when complementary donors or acceptors are available, while other classes of functional groups only occasionally participate in hydrogen bonding [135]. This discussion on the concept of best donor- and acceptor-forming H-bonds provides a cogent tool for controlling the composition and structure of molecular assemblies. Thus, novel molecular assemblies can be designed using complementary sets of strong and weak H-bonds. It is interesting to note that this competition between H-bonds in solid state mirrors those found in solution or in the gas phase.

### APPLICATIONS

There are two aspects of nanomaterial design, which is addressed in this section. These include theoretical investigations of known nanomaterials and de novo theoretical design of new nanomaterials. Apart from an awareness of intermolecular interactions, investigations of the properties of known nano-



materials provide useful information on the level of theory required to investigate nanomaterials. Thus, for example, systems containing a number of  $\pi$ -systems would require the use of theoretical methods, which explicitly include electron correlation. On the other hand, Hartree–Fock or density functional methods suffice in the investigation of systems dominated by hydrogen bonds. Though we examined each of the interaction forces in isolation in the previous section, the structure and subsequent properties of most of the nanosystems are the consequence of the cooperativity and competition of several interaction forces. With the aid of understanding of these individual interaction forces and their cooperative and competitive effect, we were able to design novel materials as well as to understand the existing functional nanomaterials.

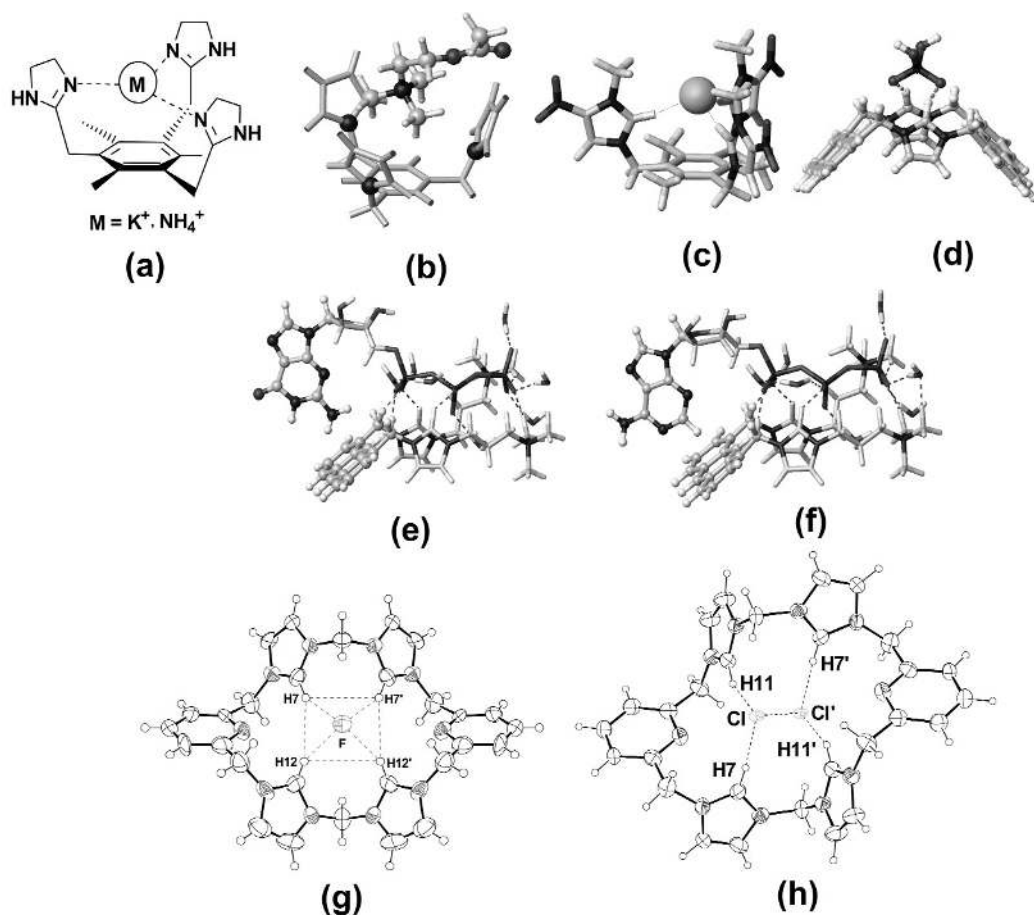
### Ionophores/receptors

The endeavors in ionophore and receptor design had its origins in developing novel receptors having potential utilities in environmental and biological systems [22,136–145]. The theoretical challenge is to describe the affinity and selectivity of the synthetic ionophore/receptors toward ions. The situation is complicated because the affinity and selectivity have to be displayed in the presence of a number of competing factors like counterions, solvents, etc. However, in order to design receptors with high affinity for a specific ion, we need to consider the enthalpy-driven interactions. In this case, the binding enthalpy is highly correlated with the binding internal energy, and so *ab initio* characterized interaction energies for an ion interacting with diverse receptors are very useful. Since we have discussed the interaction of various ions with water molecules, it is possible to replace the water molecules of the hydrated ion clusters by energetically most favorable organic moieties as the binding arms of receptor. Indeed, we have investigated the interaction energies of various ions with diverse synthetic organic receptors.

One of our initial endeavors in ionophore/receptor design was to tackle one of the seemingly intractable problems of contemporary biochemistry: the selective recognition of the ammonium cation ( $\text{NH}_4^+$ ). Much of the problem is due to the nearly equivalent sizes of  $\text{NH}_4^+$  and the potassium cation ( $\text{K}^+$ ). The first step in the receptor design was that high selectivity for  $\text{NH}_4^+$  could be achieved with cation– $\pi$  interactions, if the receptors have an optimal space to capture  $\text{NH}_4^+$  and exhibit strong interactions toward  $\text{NH}_4^+$ . However, the ionic radius of  $\text{K}^+$  is nearly similar to that of  $\text{NH}_4^+$ , so spatial differentiation is not useful. On the other hand, the difference in coordination numbers can be utilized.  $\text{K}^+$  favors coordination number of six, while  $\text{NH}_4^+$  favors only four. Furthermore, one has also to take into account the directional H-bonds involving  $\text{NH}_4^+$  cations, to describe the higher selectivity for  $\text{NH}_4^+$  over  $\text{K}^+$ . Our initial calculations indicated that a benzene-based tripodal system with dihydro-imidazole moieties (Fig. 3a) possessed vacant sites for the interaction with only one solvent molecule, while the  $\text{K}^+$  ion has three vacant sites for three solvent molecules. In order to maximize the affinity and selectivity of these receptors for  $\text{NH}_4^+$ , it becomes important to maximize the  $\pi$ -electron density of the receptor. Indeed, receptors with enhanced  $\pi$ -electron density by trimethylated phenyl ring with the strong proton-withdrawing subunits exhibit much higher affinities and selectivities [146].

Given this background, an extended concept has been applied to the receptor design for a biologically important molecule, acetylcholine [147]. The receptor should have higher affinity and selectivity for acetylcholine over  $\text{NH}_4^+$ . This requires enhanced dispersion interactions and diminished ionic interactions, which is met by replacing the imidazole arms of the  $\text{NH}_4^+$  receptors by pyrrole (Fig. 3b). These theoretical inferences were confirmed by experiments.

Interactions involving anions are very different from those of cations. Since anions are more polarizable and hence more susceptible to polar solvents than cations, it becomes important to take into account solvent effects. Based on *ab initio* calculations, highly selective anion ionophores have been designed [148,149]. Enhanced dipole moments (Fig. 3c) were employed by attaching an electron-withdrawing group. This approach would also aid design of novel functional molecular systems and biologically important chemosensors. Utilizing the  $\text{CH}^+\cdots\text{X}^-$  ionic H-bonds, fluorescent photoinduced



**Fig. 3** Receptors for  $NH_4^+$  (a), acetylcholine (b),  $Cl^-$  (c),  $H_2PO_4^-$  (d), **R1**-GTP (e), and **R1**-ATP complexes (**R1** as defined in the text) (f), crystal structure of  $F^-$ -Calix[4]imidazolium[2]pyridine (g), and  $Cl^-$ -calix[4]imidazolium[2]pyridine (h). Reproduced by permission of Springer-Verlag GmbH [45].

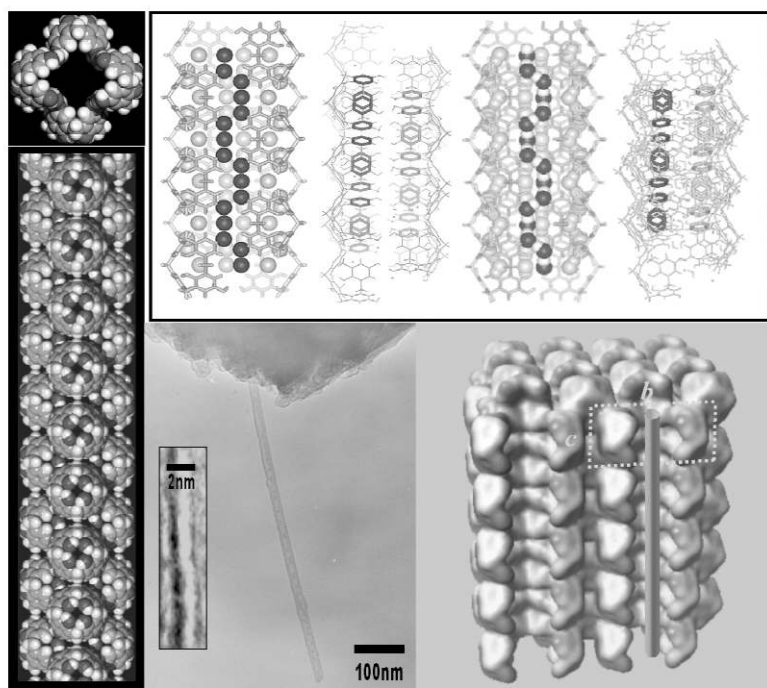
electron-transfer chemosensors for the recognition of halide anions,  $H_2PO_4^-$ , and pyrophosphate have also been designed and synthesized (Fig. 3d) [150–153]. Recently, this concept has been extended to the design of receptors (**R1**: trimethyl-[4-(3-methyl-imidazol-1-ium)-butyl]-ammonium substituted at 1,8 anthracene position) specific for the biologically important phosphates (guanosine 5'-triphosphate, GTP, and adenosine 5'-triphosphate, ATP) (Figs. 3e,f) [154] and calix-[4]-imidazolium compounds (Figs. 3g,h) [155] for selectively sensing fluoride anion. Various amphi-ionophores with cyclopeptides [156,157] and cationophores with collarenes [98,158–160] have also been designed.

### Organic nanotubes

There are several advantages of using H-bonds to design nanomaterials, and in particular organic nanotubes [161–163], because these nanotubes have potential applications as artificial biological channels, drug delivery, nanochemical reactors, nanosensors, etc. One of the interesting aspects of a recent report on the self-assembly of an organic nanotube from nontubular units of calix[4]hydroquinone (CHQ) was that the theoretical design preceded and was done in parallel with the actual experiment of synthesis and

investigation of the X-ray structure. Apart from highlighting the robustness of the theoretical approach, this study also provided several insights into the mechanism of self-assembly of CHQ nanotubes.

In the absence of water, for each CHQ monomer, the number of dangling H-atoms is 4, while in the presence of water, these dangling H-atoms of CHQs form chains  $\text{HQ}-(\text{water-HQ-HQ})_n-\text{water}$ . As the strength of 1D short hydrogen bonding interaction ( $\sim 10$  kcal/mol) is stronger than the strength of the  $\pi$ - $\pi$  stacking interaction, the assembling along the 1D short H-bonds relay is much more favorable. Indeed, in experiments with water, CHQs are assembled to form long tubular structures with four infinitely long short strong H-bond arrays. The CHQ tubes assemble to form long tubular structures in the presence of water, which in turn form bundles with intertubular  $\pi$ - $\pi$  stacking interactions, resulting in crystals with well-ordered 2D arrays of pores. A needle-like nanotube bundle exhibits the infinitely long 1D hydrogen bonding network between hydroxyl groups of CHQs and water molecules and well-ordered intertubular  $\pi$ - $\pi$  stacking pairs (Fig. 4).



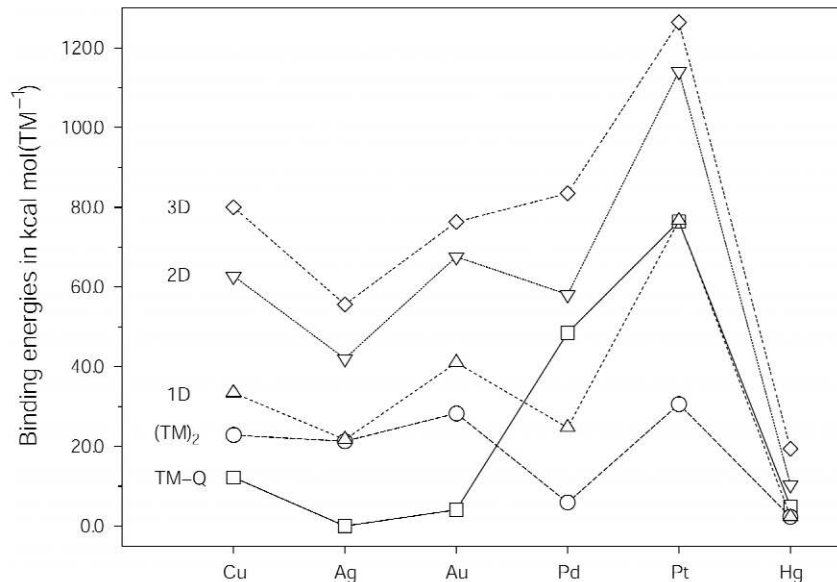
**Fig. 4** CHQ nanotubes: structure, longitudinal 1D H-bond relay vs. intertubular  $\pi$ - $\pi$  stacking, the HREM image of a single nanotube, and the water-accessible surface of the tubes. Each tube has four pillar frames of short H-bonds, and the pore size is  $8 \times 8 \text{ \AA}^2$  (in yellow). The unit cell is drawn by the dashed lines. Reproduced by permission of American Chemical Society [161,163].

As mentioned earlier, CHQ nanotube arrays can be utilized in promising templates for nanosynthesis. Redox reaction of the nanotube in the presence of silver nitrate leads to the formation of silver nanostructures, including nanoclusters, nanowires, and nanofilms. The driving force for the formation of these nanostructures is the free-energy gain due to the reduction-oxidation process [164].

The theoretical characterization of the reduced form of the CHQ nanotube was carried out using plane-wave pseudopotential methods. Our calculations indicated that upon reduction with silver nitrate, the CHQ nanotubes get transformed to the corresponding calix[4]quinone-hydroquinone (CQH) nanotubes, whose band gaps of 0.3 eV indicate that they are semiconducting in nature. The gross structural feature of CQH nanotubes is similar to that of CHQ nanotubes, with well-ordered H-bond arrays

and intertubular  $\pi$ - $\pi$  stacking pairs. In the CQHQ nanotubes, there are only two infinitely long 1D H-bond arrays per nanotube because two hydroxyl groups are transformed to the corresponding reduced forms, resulting in nanostructures.

Our recent investigation on the binding pattern of neutral and cationic transition metals with the redox system of hydroquinone (HQ) and quinone (Q) predicts what kind of nanostructures (clusters, wires, films) would form during the self-assembly process of HQ and CHQ. We could envisage that during the formation of metal nanowires from the corresponding metal salt, several competing factors are decisive for efficiency or even for mere occurrence of the redox reaction and self-synthesis. During the process, a transition-metal (TM) cation may approach either an HQ or Q moiety. To initiate the redox process, the cation must bind to HQ. Once they are interacting, HQ is oxidized to Q, while the metal cation is reduced to the neutral state. Thus, even if the necessary condition regarding  $E^0$  [ $E^0(\text{TM}^{n+}) < -0.70 \text{ V}$ ] is met, self-synthesis will only take place efficiently, as those metal cations show binding preference toward HQ over Q. More importantly, the binding of  $\text{TM}^{n+}$  with HQ is much greater than that of TM with either HQ or Q, which ensures continuous progress in the self-synthesis. In addition, the interaction energies of the neutral metals either are very weak for both ligands or clearly favor binding to Q. Hence, once the neutral metal is formed, it will not block the interaction sites of the reduced form of the ligand (i.e., HQ), such that the HQ sites are available for the remaining metal cations to be reduced to the corresponding neutrals. Furthermore, to form 1D nanowire structures, the BE of TM-Q should be smaller than (or at least comparable to) that of a 1D TM nanowire, such that aggregation is favored over formation of isolated TM atoms coordinated to Q. During the growth process, different stages of dimensionality are passed along the way from the initial dimerization step. The resulting cohesive energy per metal atom generally increases from an isolated dimer via a 1D wire and a 2D layer to the 3D bulk (Fig. 5). Therefore, an initially weak bimetallic interaction may be overcome in a final 1D or 2D metallic array, but encompasses a barrier en route to the metallic product.



**Fig. 5** Comparison of binding energies per TM for TM-Q, (TM)<sub>2</sub>, 1D, 2D, and 3D structures of the TM. Reproduced by permission of Wiley-VCH [164].

The above condition for wire formation is met for five metals Ag, Pd, Au and Pt and Hg, which satisfy the redox potential condition. In the case of Hg, we expect that the nanowire formation would

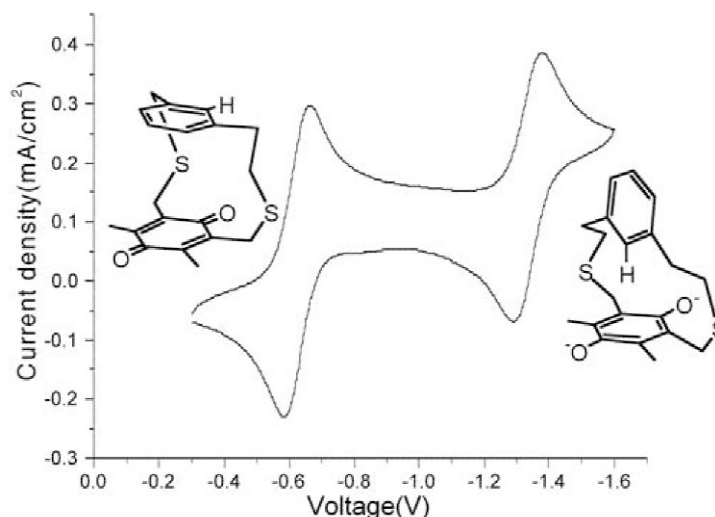
be more likely to be nanorod-like with a few atoms in the cross-section, as suggested by experiment. In the case of the Ag/Au system, the TM–Q binding energy is very weak, while the dimerization energy as well as the 1D-TM nanowire formation energy is large. This indicates that the formation of a metallic nanostructure is favored over formation of isolated metal atoms coordinated to Q moieties, resulting in effective nanowire formation. On the other hand, for the Pd system, the Pd–Q binding energy is much larger than the 1D nanowire formation energy, which forbids the nanowire formation. As a consequence, metal nanowire growth is expected to occur efficiently for Ag and Au, but not for Pd, while Pt and Hg will exhibit competing behavior between aggregation to nanowires or nanorods and attachment to the ligand. These findings were very crucial for the understanding of the self-assembly process of the TM nanowires self-synthesized by HQ and CHQ by electrochemical redox processes.

### Organic nanodevices

The quest for nanodevices implies that one has to induce motion in a system using external or internal means. The external means could include changes in pH, radiation, etc. We discuss one such device (a molecular flipper), which has been designed, synthesized, and characterized [86]. The flipping/flapping motion is due to the changes of edge-to-face and face-to-face aromatic interactions. It is interesting to note that this conformational change can be electrochemically controlled by reduction/oxidation of the Qe moiety in the molecular system.

The strategy for the design of nanodevices is to harness the subtle changes in the  $\pi$ -electron densities of a Q moiety as results of changes in the electronic environment. Quinones are particularly suited for this endeavor because their electronic characteristics can be electro- or photochemically controlled. Based on a theoretical investigation of the conformational characteristics of *p*-benzoquinone-benzene complexes, we found that the energy difference between the stacked and edge-to-face conformations of cyclophane molecules is substantial. Thus, if one could subtly control the conformational characteristics of 2,11-dithio[4,4]metametaquinocyclophane (MQC) (stacked conformer is 7 kcal/mol more stable than the edge-to-face conformer) and 2,11-dithio[4,4]metametahydroquinocyclophane (MHQC) (edge-to-face is 9 kcal/mol more stable than the stacked conformer) by electrochemical and/or photochemical means, we can have a very interesting model of a potential molecular device. The cyclic voltammograms of MQC exhibits two clear reversible redox reactions (Fig. 6). In aprotic media, Qs exhibit two reduction peaks separated by 0.7 V, which corresponds to the formation of a radical anion species and a dianion species of Qs, respectively. This is in agreement with the reduction characteristics of MQC. Two well-separated reduced states of MQC are formed in the aprotic solvent of acetonitrile upon reduction. Therefore, the electronic states of MQC and MHQC can be easily transformed into each other by simple electrochemical control of the redox reaction, which results in large conformational flapping motions due to a preference for the stable conformation caused by the change in the electronic state of the Q moiety.

Thus, a cyclophane system composed of Q and benzene rings exhibits a flapping motion involving squeezing and thrusting motions in the presence of solvent molecules by electrochemical redox process. This case illustrates a promising pathway of harnessing the differences in the relative magnitudes of different kinds of intermolecular interactions to design a nanomechanical device. The large flapping/flipping motion from the edge-to-face and stacked conformations and vice versa is a first step toward a propelling molecular vessel or a molecular flipper that can be electrochemically or photochemically controlled. It could be applied to the design of molecular hinges, molecular switches, and eventually to the design of mobile nanomechanical devices for drug delivery and nanosurgery.



**Fig. 6** Cyclic voltammogram of MHQC(left)/MQC(right) (1 mM) in acetonitrile with tetrabutylammonium dihydrogen phosphate (0.1 M) at 25 °C (scan rate 100 mV/s). Reproduced by permission of American Chemical Society [86].

## CONCLUSION

In this review, we have illustrated our efforts toward understanding the theoretical principles of nanorecognition, and de novo design approach toward the nanomaterial design using a wide variety of examples. Apart from stressing the strengths and weaknesses of several theoretical methodologies, our extensive studies also highlight that an understanding of intermolecular interactions is very useful in nanomaterial design. Theoretical calculations involving nanomaterials should explicitly take into account electron correlation. Apart from providing accurate estimates of dispersion energies, which are widely prevalent in nanomaterials, the inclusion of electron correlation also influences the magnitude of other interaction energy components like induction energies. In systems involving a large number of atoms, it is computationally not feasible to use very high-level theoretical methodologies. In such a case, the use of density functional or semi-empirical methods is advocated. However, adequate care should be taken while interpreting the results. The magnitude of repulsive energies is very important in that the equilibrium structures of most nanomaterials are the ones wherein the interaction energies (the sum of attractive energies and repulsive energies) are maximized. Quantitative estimates of the magnitudes of various intermolecular interactions and energy components are very useful in determining their relative importance. However, weak interactions are of importance in the sense that they steer and promote much stronger interactions. Given the success of our approach in designing experimentally viable nanomaterials, we believe that the coming years would see the use of this approach in the development of novel nanosystems with potential applications in pharmaceuticals, optics, opto-electronics, information storage, sensors, biotechnology, nanomedicine, nanofluidics, and nanoelectronics. Furthermore, it would also provide vital information on the methods needed to harness these nanosystems as machines and devices and provide an increased understanding of the science behind most nanoscale processes.

## ACKNOWLEDGMENT

This work was supported by GRL (KICOS) and BK21.

## REFERENCES

1. K. S. Kim, P. Tarakeshwar, H. M. Lee. In *Dekker Encyclopedia of Nanoscience and Nanotechnology*, Vol. 3, J. A. Schwarz, C. Contescu, K. Putyera (Eds.), pp. 2423–2433, Marcel Dekker, New York (2003).
2. P. Tarakeshwar, K. S. Kim. In *Encyclopedia of Nanoscience and Nanotechnology*, Vol. 7, H. S. Nalwa (Ed.), pp. 367–404, American Science Publishers, California (2003).
3. P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, P. R. Schreiner (Eds.). *Encyclopedia of Computational Chemistry*, John Wiley, Chichester (1998).
4. C. E. Dykstra, G. Frenking, K. S. Kim, G. Scuseria (Eds.). *Theory and Applications of Computational Chemistry: The First 40 Years, A Volume of Technical and Historical Perspectives*, Elsevier, Amsterdam (2005).
5. H. Kuhn, H.-D. Försterling. *Principles of Physical Chemistry: Understanding Molecules, Molecular Assemblies and Supramolecular Machines*, John Wiley, New York (1999).
6. J. Leszczynski (Ed.). *Computational Material Science*, Elsevier, Amsterdam (2003).
7. K. D. Shen (Ed.). *Reviews in Modern Quantum Chemistry*, World Scientific, Singapore (2002).
8. K. S. Kim, P. Tarakeshwar, J. Y. Lee. *Chem. Rev.* **100**, 4145 (2000).
9. H. F. Schaefer III (Ed.). *Methods of Electronic Structure Theory*, Plenum, New York (1977).
10. K. Szalewicz, B. Jeziorski. In *Molecular Interactions: From van der Waals to Strongly Bound Complexes*, S. Scheiner (Ed.), p. 3, John Wiley, New York (1997).
11. H. M. Lee, M. Ge, B. R. Sahu, P. Tarakeshwar, K. S. Kim. *J. Phys. Chem. B* **107**, 9994 (2003).
12. T. Nautiyal, T. H. Rho, K. S. Kim. *Phys. Rev. B* **69**, 193404 (2004).
13. D. Cheng, W. Y. Kim, S. K. Min, T. Nautiyal, K. S. Kim. *Phys. Rev. Lett.* **96**, 096104 (2006).
14. S. Scheiner. *Hydrogen Bonding: A Theoretical Perspective*, University Press, Oxford (1997).
15. G. A. Jeffrey. In *An Introduction to Hydrogen Bonding*, D. Truhlar (Ed.), Oxford University Press, New York (1997).
16. M. Ziolkowski, S. J. Grabowski, J. Leszczynski. *J. Phys. Chem. A* **110**, 6514 (2006).
17. S. J. Grabowski, W. A. Sokalski, J. Leszczynski. *J. Phys. Chem. A* **110**, 4772 (2006).
18. C. Pak, H. M. Lee, J. C. Kim, D. Kim, K. S. Kim. *Struct. Chem.* **16**, 187 (2005).
19. K. S. Kim, B. J. Mhin, U.-S. Choi, K. Lee. *J. Chem. Phys.* **97**, 6649 (1992).
20. H. M. Lee, S. B. Suh, J. Y. Lee, P. Tarakeshwar, K. S. Kim. *J. Chem. Phys.* **112**, 9759 (2000).
21. J. Kim, K. S. Kim. *J. Chem. Phys.* **109**, 5886 (1998).
22. J. Yoon, S. K. Kim, N. J. Singh, K. S. Kim. *Chem. Soc. Rev.* **35**, 355 (2006).
23. H. M. Lee, P. Tarakeshwar, J. W. Park, M. R. Kolaski, Y. J. Yoon, H.-B. Yi, W. Y. Kim, K. S. Kim. *J. Phys. Chem. A* **108**, 2949 (2004).
24. A. Veerman, H. M. Lee, K. S. Kim. *J. Chem. Phys.* **123**, 084321 (2005).
25. J. Kim, H. M. Lee, S. B. Suh, D. Majumdar, K. S. Kim. *J. Chem. Phys.* **113**, 5259 (2000).
26. D. Majumdar, J. Kim, K. S. Kim. *J. Chem. Phys.* **112**, 101 (2000).
27. S. B. Suh, J. C. Kim, Y. C. Choi, S. Yun, K. S. Kim. *J. Am. Chem. Soc.* **126**, 2186 (2004).
28. W. W. Cleland, M. M. Krevoy. *Science* **264**, 1887 (1994).
29. P. A. Frey. *Science* **269**, 104 (1995).
30. K. S. Kim, K. S. Oh, J. Y. Lee. *Proc. Natl. Acad. Sci. USA* **97**, 6373 (2000).
31. 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. *Biochemistry* **39**, 13891 (2000).
32. K. S. Kim, D. Kim, J. Y. Lee, P. Tarakeshwar, K. S. Oh. *Biochemistry* **41**, 5300 (2002).
33. T. K. Manojkumar, C. Cui, K. S. Kim. *J. Comput. Chem.* **26**, 606 (2005).
34. S. K. Burley, G. A. Petsko. *Science* **229**, 23 (1985).
35. B. Brutschy. *Chem. Rev.* **100**, 3891 (2000).
36. P. Tarakeshwar, H. S. Choi, K. S. Kim, S. Djafari, K. Buchhold, B. Reimann, H.-D. Barth, B. Brutschy. *J. Chem. Phys.* **114**, 4016 (2001).

37. S. Vaupel, B. Brutschy, P. Tarakeshwar, K. S. Kim. *J. Am. Chem. Soc.* **128**, 5416 (2006).
38. S. Scheiner, T. Kar, J. Pattanayak. *J. Am. Chem. Soc.* **124**, 13257 (2002).
39. R. Ren, Y. Jin, K. S. Kim, D. H. Kim. *J. Biomol. Struct. Dyn.* **15**, 401 (1997).
40. B. H. Hong, J. Y. Lee, S. J. Cho, S. Yun, K. S. Kim. *J. Org. Chem.* **64**, 5661 (1999).
41. P. Tarakeshwar, H. S. Choi, S. J. Lee, J. Y. Lee, K. S. Kim, T.-K. Ha, J. H. Jang, J. G. Lee, H. Lee. *J. Chem. Phys.* **111**, 5838 (1999).
42. K. S. Kim, J. Y. Lee, H. S. Choi, J. Kim, J. H. Jang. *Chem. Phys. Lett.* **265**, 497 (1997).
43. P. Hobza, H. L. Selzle, E. W. Schlag. *Chem. Rev.* **94**, 1767 (1994).
44. P. Hobza, H. L. Selzle, E. W. Schlag. *J. Chem. Phys.* **93**, 5893 (1990).
45. N. J. Singh, A. C. Olleta, Anupriya, M. Park, H.-B. Yi, I. Bandyopadhyay, H. M. Lee, P. Tarakeshwar, K. S. Kim. *Theor. Chem. Acc.* **115**, 127 (2006).
46. J. Kim, S. Lee, S. J. Cho, B. J. Mhin, K. S. Kim. *J. Chem. Phys.* **102**, 839 (1995).
47. S. Lee, J. Kim, J. K. Park, K. S. Kim. *J. Phys. Chem.* **100**, 14329 (1996).
48. H. M. Lee, J. Kim, S. Lee, B. J. Mhin, K. S. Kim. *J. Chem. Phys.* **111**, 3995 (1999).
49. (a) N. J. Singh, M. Park, S. K. Min, S. B. Suh, K. S. Kim. *Angew. Chem., Int. Ed.* **45**, 3795 (2006);  
(b) N. J. Singh, M. Park, S. K. Min, S. B. Suh, K. S. Kim. *Angew. Chem.* **118**, 3879 (2006).
50. J. Baik, J. Kim, D. Majumdar, K. S. Kim. *J. Chem. Phys.* **110**, 9116 (1999).
51. H. M. Lee, K. S. Kim. *J. Chem. Phys.* **114**, 4461 (2001).
52. H. M. Lee, P. Tarakeshwar, K. S. Kim. *J. Chem. Phys.* **121**, 4657 (2004).
53. A. Kammrath, J. R. R. Verlet, A. E. Bragg, G. B. Griffin, D. M. Neumark. *J. Phys. Chem. A* **109**, 11475 (2005).
54. B. Gao, Z.-F. Liu. *J. Phys. Chem. A* **109**, 9104 (2005).
55. R. Lian, D. A. Oulianov, R. A. Crowell, I. A. Shkrob, X. Chen, S. E. Bradforth. *J. Phys. Chem. A* **110**, 9071 (2006).
56. S. Odde, C. Pak, H. M. Lee, K. S. Kim, B. J. Mhin. *J. Chem. Phys.* **121**, 204 (2004).
57. J. Park, M. Kolaski, H. M. Lee, K. S. Kim. *J. Chem. Phys.* **121**, 3108 (2004).
58. E. C. Lee, H. M. Lee, P. Tarakeshwar, K. S. Kim. *J. Chem. Phys.* **119**, 7725 (2003).
59. H. M. Lee, S. K. Min, E. C. Lee, J. H. Min, S. Odde, K. S. Kim. *J. Chem. Phys.* **122**, 064314 (2005).
60. H. M. Lee, M. Diefenbach, S. B. Suh, P. Tarakeshwar, K. S. Kim. *J. Chem. Phys.* **123**, 074328 (2005).
61. S. Odde, B. J. Mhin, S. Lee, H. M. Lee, K. S. Kim. *J. Chem. Phys.* **120**, 9524 (2004).
62. A. C. Olleta, H. M. Lee, K. S. Kim. *J. Chem. Phys.* **124**, 024321 (2006).
63. N. J. Singh, H.-B. Yi, S. K. Min, M. Park, K. S. Kim. *J. Phys. Chem. B* **110**, 3808 (2006).
64. E. A. Meyer, R. K. Castellano, F. Diederich. *Angew. Chem., Int. Ed.* **42**, 1210 (2003).
65. B. H. Hong, J. P. Small, M. S. Purewal, A. Mullokandov, M. Y. Sfeir, F. Wang, J. Y. Lee, T. F. Heinz, L. E. Brus, P. Kim, K. S. Kim. *Proc. Nat. Acad. Sci. USA* **102**, 14155 (2005).
66. K. S. Kim. *Bull. Korean Chem. Soc.* **24**, 757 (2003).
67. F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning. *Chem. Rev.* **105**, 1491 (2005).
68. P. Hobza, J. Šponer. *J. Am. Chem. Soc.* **124**, 11802 (2002).
69. K. Müller-Dethlefs, P. Hobza. *Chem. Rev.* **100**, 143 (2000).
70. O. Engkvist, P. Hobza, H. L. Selzle, E. W. Schlag. *J. Chem. Phys.* **110**, 5758 (1999).
71. C. A. Hunter, J. K. M. Sanders. *J. Am. Chem. Soc.* **112**, 5525 (1990).
72. C. A. Hunter. *Angew. Chem., Int. Ed.* **32**, 1584 (1993).
73. C. A. Hunter. *Chem. Soc. Rev.* **23**, 101 (1994).
74. F. J. Carver, C. A. Hunter, D. J. Livingstone, J. F. McCabe, E. M. Seward. *Chem. Eur. J.* **8**, 2848 (2002).
75. F. Cozzi, M. Cinquini, R. Annunziata, T. Dwyer, J. S. Siegel. *J. Am. Chem. Soc.* **114**, 5729 (1992).
76. F. Cozzi, R. Annunziata, M. Benagliz, M. Cinquini, L. Raimondi, K. K. Baldrige, J. S. Siegel. *Org. Biomol. Chem.* **1**, 157 (2003).



77. E. C. Lee, B. H. Hong, J. Y. Lee, J. C. Kim, D. Kim, Y. Kim, P. Tarakeshwar, K. S. Kim. *J. Am. Chem. Soc.* **127**, 4530 (2005).
78. P. Tarakeshwar, H. S. Choi, K. S. Kim. *J. Am. Chem. Soc.* **123**, 3323 (2001).
79. T. K. Manojkumar, H. S. Choi, B. H. Hong, P. Tarakeshwar, K. S. Kim. *J. Chem. Phys.* **121**, 841 (2004).
80. I. Bandyopadhyay, H. M. Lee, K. S. Kim. *J. Phys. Chem. A* **109**, 1720 (2005).
81. M. O. Sinnokrot, E. F. Valeev, C. D. Sherrill. *J. Am. Chem. Soc.* **124**, 10887 (2002).
82. M. O. Sinnokrot, C. D. Sherrill. *J. Am. Chem. Soc.* **126**, 7690 (2004).
83. G. Karlström, P. Linse, A. Wallqvist, B. Jönsson. *J. Am. Chem. Soc.* **105**, 3777 (1983).
84. S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe. *J. Am. Chem. Soc.* **124**, 104 (2002).
85. T. Sato, T. Tsuneda, K. Hirao. *J. Chem. Phys.* **123**, 104307 (2005).
86. 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. *Org. Lett.* **4**, 3971 (2002).
87. T. K. Manojkumar, D. Kim, K. S. Kim. *J. Chem. Phys.* **122**, 014305 (2005).
88. K. S. Kim, J. Y. Lee, S. J. Lee, T.-K. Ha, D. H. Kim. *J. Am. Chem. Soc.* **116**, 7399 (1994).
89. J. Y. Lee, S. J. Lee, H. S. Choi, S. J. Cho, K. S. Kim, T. K. Ha. *Chem. Phys. Lett.* **232**, 67 (1995).
90. D. Kim, S. Hu, P. Tarakeshwar, K. S. Kim, J. M. Lisy. *J. Phys. Chem. A* **107**, 1228 (2003).
91. P. Tarakeshwar, K. S. Kim, E. Kraka, D. Cremer. *J. Chem. Phys.* **115**, 6018 (2001).
92. P. Tarakeshwar, S. J. Lee, J. Y. Lee, K. S. Kim. *J. Chem. Phys.* **108**, 7217 (1998).
93. P. Tarakeshwar, J. Y. Lee, K. S. Kim. *J. Phys. Chem. A* **102**, 2253 (1998).
94. D. A. Dougherty, D. Stauffer. *Science* **250**, 1558 (1990).
95. R. A. Kumpf, D. A. Dougherty. *Science* **261**, 1708 (1993).
96. J. C. Ma, D. A. Dougherty. *Chem. Rev.* **97**, 1303 (1997).
97. J. P. Gallivan, D. A. Dougherty. *J. Am. Chem. Soc.* **122**, 870 (2000).
98. H. S. Choi, S. B. Suh, S. J. Cho, K. S. Kim. *Proc. Natl. Acad. Sci. USA* **95**, 12094 (1998).
99. J. Sunner, K. Nishizawa, P. Kebarle. *J. Phys. Chem.* **85**, 1814 (1981).
100. M. Meot-Ner (Mautner), L. W. Sieck. *J. Phys. Chem.* **89**, 5222 (1985).
101. J. W. Caldwell, P. A. Kollman. *J. Am. Chem. Soc.* **117**, 4177 (1995).
102. A. Pullman, G. Berthier, R. Savinelli. *J. Am. Chem. Soc.* **120**, 8553 (1998).
103. V. Ryzhov, R. C. Dunbar. *J. Am. Chem. Soc.* **121**, 2259 (1999).
104. S. L. De Wall, E. S. Meadows, L. J. Barbour, G. W. Gokel. *J. Am. Chem. Soc.* **121**, 5613 (1999).
105. J. B. Nicholas, B. P. Hay, D. A. Dixon. *J. Phys. Chem. A* **104**, 11414 (2000).
106. D. M. Quinn, S. R. Feaster, H. K. Nair, N. A. Baker, Z. Radić, P. Taylor. *J. Am. Chem. Soc.* **122**, 2975 (2000).
107. T. Kar, R. Ponc, A. B. Sannigrahi. *J. Phys. Chem. A* **105**, 7737 (2001).
108. T. Liu, J. Gu, X.-J. Tan, W.-L. Zhu, X.-M. Luo, H.-L. Jiang, R.-Y. Ji, K.-X. Chen, I. Silman, J. L. Sussman. *J. Phys. Chem. A* **105**, 5431 (2001).
109. C. Chipot, F. Dehez, J. Ángyán, C. Millot, M. Orozco, F. J. Luque. *J. Phys. Chem. A* **105**, 11505 (2001).
110. F. M. Siu, N. L. Ma, C. W. Tsang. *J. Am. Chem. Soc.* **123**, 3397 (2001).
111. Y. Mo, G. Subramanian, J. Gao, D. M. Ferguson. *J. Am. Chem. Soc.* **124**, 4832 (2002).
112. D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa, P. M. Déya. *Angew. Chem., Int. Ed.* **41**, 3389 (2002).
113. M. Mascal, A. Armstrong, M. D. Bartberger. *J. Am. Chem. Soc.* **124**, 6274 (2002).
114. I. Alkorta, I. Rozas, J. Elguero. *J. Am. Chem. Soc.* **124**, 8593 (2002).
115. M. Mascal. *Angew. Chem., Int. Ed.* **45**, 2890 (2006).
116. O. B. Berryman, F. Hof, M. J. Hynes, D. W. Johnson. *Chem. Commun.* 506 (2006).
117. D. Kim, P. Tarakeshwar, K. S. Kim. *J. Phys. Chem. A* **108**, 1250 (2004).
118. M. I. Cabaco, Y. Danten, M. Besnard, Y. Guissani, B. Guillot. *J. Phys. Chem. B* **102**, 10712 (1998).

119. A. P. West Jr., S. Mecozzi, D. A. Dougherty. *J. Phys. Org. Chem.* **10**, 347 (1997).
120. A. Karpfen. *J. Phys. Chem. A* **103**, 11431 (1999).
121. B. H. Cardelino, C. E. Moore, D. O. Frazier, D. G. Musaev, K. Morokuma. *Int. J. Quantum Chem.* **66**, 189 (1998).
122. M. C. Chan, P. A. Block, R. E. Miller. *J. Chem. Phys.* **102**, 3993 (1995).
123. H. Krause, B. Ernstberger, H. J. Neusser. *Chem. Phys. Lett.* **184**, 411 (1991).
124. J. R. Grover, E. A. Walters, E. T. Hui. *J. Phys. Chem.* **91**, 3233 (1987).
125. Y. C. Choi, W. Y. Kim, K.-S. Park, P. Tarakeshwar, K. S. Kim, T.-S. Kim, J. Y. Lee. *J. Chem. Phys.* **122**, 094706 (2005).
126. H. M. Lee, S. B. Suh, P. Tarakeshwar, K. S. Kim. *J. Chem. Phys.* **122**, 044309 (2005).
127. H. M. Lee, S. Lee, K. S. Kim. *J. Chem. Phys.* **119**, 187 (2003).
128. S. B. Suh, H. M. Lee, J. Kim, J. Y. Lee, K. S. Kim. *J. Chem. Phys.* **113**, 5273 (2000).
129. K. S. Kim, S. Lee, J. Kim, J. Y. Lee. *J. Am. Chem. Soc.* **119**, 9329 (1997).
130. D. Majumdar, H. M. Lee, J. Kim, K. S. Kim. *J. Chem. Phys.* **111**, 5866 (1999).
131. M. Kolaski, H. M. Lee, C. Pak, M. Dupuis, K. S. Kim. *J. Phys. Chem. A* **109**, 9419 (2005).
132. H. M. Lee, J. Kim, C.-J. Kim, K. S. Kim. *J. Chem. Phys.* **116**, 6549 (2002).
133. J. M. Park, P. Tarakeshwar, K. S. Kim, T. Clark. *J. Chem. Phys.* **116**, 10684 (2002).
134. Y. C. Choi, W. Y. Kim, K.-S. Park, P. Tarakeshwar, K. S. Kim, T.-S. Kim, J. Y. Lee. *J. Chem. Phys.* **122**, 094706 (2005).
135. D. N. Chin, J. A. Zerkowski, J. C. MacDonald, G. M. Whitesides. In *Organized Molecular Assemblies in the Solid State*, J. K. Whitesell (Ed.), p. 185, John Wiley, New York (1999).
136. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn. *Comprehensive Supramolecular Chemistry*, Vols. 1–11, Elsevier, Amsterdam (1996).
137. J. L. Sessler, D. Seidel. *Angew. Chem., Int. Ed.* **42**, 5134 (2003).
138. T. S. Snowden, E. V. Anslyn. *Chem. Biol.* **3**, 740 (1999).
139. *Supramolecular Chemistry of Anions*, A. Bianchi, K. Bowman-James, E. García-España (Eds.), Wiley-VCH, New York (1997).
140. P. de Hoog, P. Gamez, I. Mutikainen, U. Turpeinen, J. Reedijk. *Angew. Chem., Int. Ed.* **43**, 815 (2004).
141. P. A. Gale. *Coord. Chem. Rev.* **240**, 191 (2003).
142. P. D. Beer, P. A. Gale. *Angew. Chem., Int. Ed.* **40**, 486 (2001).
143. F. P. Schmidtchen, M. Berger. *Chem. Rev.* **97**, 1609 (1997).
144. D. M. Rudkevich, Z. Brzozka, M. Palys, H. C. Visser, W. Verboom, D. N. Reinhoudt. *Angew. Chem., Int. Ed.* **33**, 467 (1994).
145. R. Martínez-Máñez, F. Sancanón. *Chem. Rev.* **103**, 4419 (2003).
146. K. S. Oh, C.-W. Lee, H. S. Choi, S. J. Lee, K. S. Kim. *Org. Lett.* **2**, 2679 (2000).
147. 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, K. S. Kim. *Org. Lett.* **5**, 471 (2003).
148. H. Ihm, S. Yun, H. G. Kim, J. K. Kim, K. S. Kim. *Org. Lett.* **4**, 2897 (2002).
149. S. Yun, H. Ihm, 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. *J. Org. Chem.* **68**, 2467 (2003).
150. S. K. Kim, N. J. Singh, S. J. Kim, H. G. Kim, J. K. Kim, J. W. Lee, K. S. Kim, J. Yoon. *Org. Lett.* **5**, 2083 (2003).
151. J. Yoon, S. K. Kim, N. J. Singh, J. W. Lee, Y. J. Yang, K. Chellappan, K. S. Kim. *J. Org. Chem.* **69**, 581 (2004).
152. S. K. Kim, N. J. Singh, S. J. Kim, K. M. K. Swamy, S. H. Kim, K. H. Lee, K. S. Kim, J. Yoon. *Tetrahedron* **61**, 4545 (2005).
153. S. K. Kim, N. J. Singh, J. Kwon, I.-C. Hwang, S. J. Park, K. S. Kim, J. Yoon. *Tetrahedron* **62**, 6065 (2006).

154. J. Y. Kwon, N. J. Singh, H. N. Kim, S. K. Kim, K. S. Kim, J. Yoon. *J. Am. Chem. Soc.* **126**, 8892 (2004).
155. (a) K. Chellapan, N. J. Singh, I. C. Hwang, J. W. Lee, K. S. Kim. *Angew. Chem., Int. Ed.* **44**, 2899 (2005); (b) K. Chellapan, N. J. Singh, I. C. Hwang, J. W. Lee, K. S. Kim. *Angew. Chem.* **117**, 2959 (2005).
156. S. B. Suh, C. Cui, H. S. Son, J. S. U, Y. Won, K. S. Kim. *J. Phys. Chem. B* **106**, 2061 (2002).
157. K. S. Kim, C. Cui, S. J. Cho. *J. Phys. Chem. B* **102**, 461 (1998).
158. (a) H. S. Choi, K. S. Kim. *Angew. Chem., Int. Ed.* **38**, 2256 (1999); (b) H. S. Choi, K. S. Kim. *Angew. Chem.* **111**, 2400 (1999).
159. S. J. Cho, H. Hwang, J. M. Park, K. S. Oh, K. S. Kim. *J. Am. Chem. Soc.* **118**, 485 (1996).
160. H. S. Choi, D. Kim, P. Tarakeshwar, S. B. Suh, K. S. Kim. *J. Org. Chem.* **67**, 1848 (2002).
161. B. H. Hong, J. Y. Lee, C.-W. Lee, J. C. Kim, K. S. Kim. *J. Am. Chem. Soc.* **123**, 10748 (2001).
162. B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong, K. S. Kim. *Science* **294**, 348 (2001).
163. 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, J.-H. Cho. *J. Am. Chem. Soc.* **124**, 14268 (2002).
164. H.-B. Yi, M. Diefenbach, Y. C. Choi, E. C. Lee, H. M. Lee, B. H. Hong, K. S. Kim. *Chem Eur. J.* **12**, 4885 (2006).