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N. Jiten Singh[a]; Han Myoung Lee[a]; In-Chul Hwang[a]; Kwang S. Kim[a]
[a] Department of Chemistry, Center for Superfunctional Materials, Pohang University of Science and Technology, Pohang, South Korea

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Designing Ionophores and Molecular Nanotubes Based on Molecular Recognition

N. JITEN SINGH, HAN MYOUNG LEE, IN-CHUL HWANG and KWANG S. KIM*

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

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In this mini-review we briefly describe intermolecular interactions ranging from hydrogen bonding to ionic interactions to aromatic interactions. Manifestation of these interaction forces is in the design and realization of various ionophores with chemo-sensing capability for biologically important cations and anions. We also explain how the understanding of hydrogen bonding and π-interactions has led to the design of self-assembled organic nanotubes. We further discuss the conformational changes between stacked and edge-to-face conformers in benzoquinone-benzene complexes, which are controlled by alternating electrochemical potential. The resulting flapping motion illustrates a promising pathway toward the design of nanomechanical devices.

Keywords: Ionophores; Receptors; Imidazolium; Nanotubes; Self-assembly; Molecular recognition

INTRODUCTION

Our interest in intermolecular interactions stems from their importance in understanding ion solvation phenomena, molecular recognition, ionophore and receptor design, ion mediated self-assembly, and nanomaterial design [1–7]. This understanding helps foresee or predict the chemical and physical properties of receptors and novel nanomaterials. Over the past decades, experimental synthesis and measurements based on intuition, experiences and trial and error approach have made important contributions in designing functional molecules and nanomaterials. However, as the systems become smaller and smaller, nanosystems involve the quantum nature of the atoms/molecules in the material, features that are hardly comprehensible by intuition and simple experience. Therefore, exploitation of commonsense alone has been limited, and a paradigm shift toward the non-intuitive design approach is highly demanding. 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 [2,3]. In this regard, computational methods, apart from providing unique insights into experimental data, have become the guiding tools towards the design of receptors and new materials with unique and important properties [2]. 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 for a given set of molecular systems, and selective recognition of ionic/molecular species by novel receptors.

In the course of this mini-review, we will briefly discuss different types of intermolecular interactions whose relevance is important to the *de-novo* design of ionophores, nanomaterials, and nanodevices. Thus, a manifestation of these intermolecular interactions is the computer-aided design of novel ionophores/receptors, endo/exohedral fullerenes, fullerides, nanotori, nanotubes, nanowires, and molecular devices. Here we discuss some representative examples related to the field of supramolecular chemistry from the works carried out in our group.

*Corresponding author. E-mail: kim@postech.ac.kr

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INTERMOLECULAR INTERACTIONS

Though various intermolecular interactions prevail in chemical and biological systems, they can be broadly classified into five different types: (i) hydrogen bonding, (ii) ionic interactions, (iii) intermolecular interactions involving π systems, (iv) metallic interactions, and (v) interactions involving quantum species. The physical properties of most receptors, molecular self assembled motifs and nanomaterials are a reflection or the result of the judicious combination of several of these intermolecular interactions, which can be either cooperative or competitive. Here, we briefly describe the main essence of these intermolecular interactions based on our theoretical investigations. Though metallic interaction [8–10] is also an important force as related to nanowires and nanomaterials, we will not consider this interaction force within the scope of this overview.

Hydrogen Bonding

Hydrogen bond (H-bond) is arguably the most vital interaction force in biology and chemistry [11,12]. For instance, both water, which is the most abundant and essential substance on our planet, and proteins/DNAs which are among the most important substances in biosystems, are held together by networks of H-bonds. The H-bond energy ranges from 2–20 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 [13]. 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, and (iii) the assembly is often fast and specific.

In general, a contribution from electrostatic energies is a key characteristic of hydrogen bonding. 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 involves multiple hydrogen bonds, cooperativity is a characteristic feature that has important consequences in receptor and nanomaterial design. For example, in water clusters, the average energy of a hydrogen bond progressively increases with an increase in the cluster size [14,15]. This enhancement in the interaction energies leads to a progressive decrease in the intermolecular hydrogen bond distance and hence significant geometry changes are usually seen.

In addition, we need to consider special types of hydrogen bonds such as ionic hydrogen bonds [16], positively charged hydrogen bonds [17,18], negatively charged hydrogen bonds [19,20], short hydrogen bonds [21], short strong hydrogen bonds [22–27], and aromatic hydrogen bonds (π–H interactions) [28–35].

Ionic Interactions

Intermolecular interactions involving ionic species are dominated by the electrostatic energies. The cation–anion interactions are ionic interactions. However, when, these ionic species are solvated, the cations and anions are dissociated. Interestingly, a noticeable difference is observed in the solvation of cationic and anionic species as a result of the fact that intermolecular interactions between these ions and solvent molecules dominate. The cation interacts with the anionic site of the solvent, resulting in the cation–dipole interaction. The contribution of electrostatic interactions toward the solvation energy of anions is 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 make itself stabilized simply due to the uncertainty principle [36]. Thus, the anion interacts with ligands on one side, while the density of the excess electron populates in an empty space on the opposite side to the ligands (Fig. 1). This is anionic H-bond interaction, i.e., anion–dipole interaction through H-bond). Furthermore, while cations prefer to interact with heavy non-hydrogen atoms (such as oxygen and nitrogen) [37–44], anions interact with the smaller-sized hydrogen atoms [45–50]. As a consequence, the electron clouds of the anion are anisotopically and directionally polarized toward the electron acceptor sites (in most cases, hydrogen atoms). Full coordination is therefore difficult to achieve in the case of anion solvation, as the columbic repulsion between crowded hydrogen atoms of solvent molecules or ligands prevents them from coming close to one another. These intriguing phenomena are useful in areas, ranging from nanoclusters to guest–host complexes [51–53] and will be discussed in the subsequent sections.

Intermolecular Interactions Involving π Systems

Interactions involving π systems [54–60] are most relevant to the problem of nanomaterial design and to a great extent to the issues of receptor design and molecular assembly [61–67]. As these interactions are perceptibly weak and difficult to observe experimentally, accurate descriptions from very

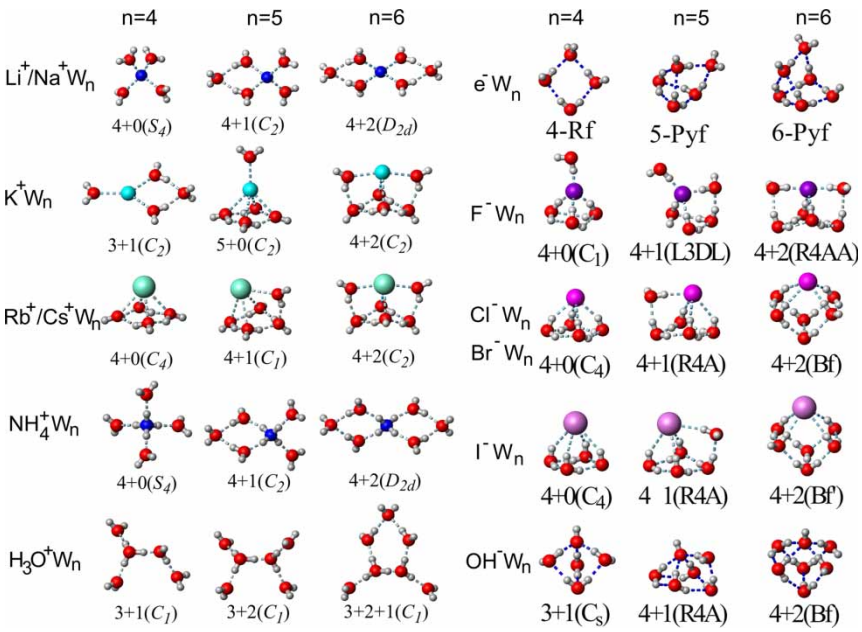

FIGURE 1 Structures of the $M{\cdot}(H_2O)_{3-6}$ complexes ($M =$ Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, H_3O^+ as cationic species and $M =$ e-, F^-, Cl^-, Br^-, I^-, OH^- as anionic species).

high level of theory are required [68–74]. A large number of systems ranging from fullerenes to ionophores to supramolecular assembly exhibit these interactions.

A broad classification of the nature of the interactions involving these π systems can be based on the nature of the countermolecules 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 π electron cloud, the polarizability of the π system is important. In the binding of the tetramethyl ammonium and ammonium cation to benzene, the dispersion energy is important [75–77]. Dispersion energies predominate when the countermolecule is either a rare gas atom or a nonpolar molecule (gas dimers, hydrocarbons) [78]. When the countermolecule is either a polar molecule or Lewis acid, both electrostatic and dispersion energies govern the interaction [79,80]. The magnitude of the repulsive energies plays a vital role in governing the observed geometry of the π system. It can be noted here that the magnitudes of the electrostatic and induction energies in the case of the organic cation complexes of these π systems are much smaller than those observed in the case of the π–alkali metal cation complexes, where the contribution of dispersion energies becomes vital. For anion–π complexes, the total interaction energies [81] are comparable to those corresponding to cation–π complexes. The characteristic feature of the anion–π interaction is the increase in the magnitude of exchange-repulsion energy due to the increased repulsion between the electron density of an aromatic ring and the electron density of an anion. However, electrostatic and induction energies as well as dispersion energies also increase. When the anion is an organic moiety, the contribution from the dispersion energies is very significant. It is interesting to note that many anion receptors have augmented anion binding affinities due to the presence of aromatic ring moieties, which interact with the anions (anion–π interactions [81–86]) in addition to other binding motifs.

While comparing the cation–water interactions with cation–π interactions [75–77,87–96], the distinction between them lies in the magnitude of the electrostatic energies, which are dominant contributors to the total interaction energies (Fig. 2). In the context of receptor and 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 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 cancel out. However the ammonium cation complexes exhibit a larger contribution of dispersion energies [75,77]. 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. Complexes exhibiting π–H interactions are of interest because this interaction is also a hydrogen bond. In going from CH_4 to NH_3, to H_2O, to HF, the increase in the

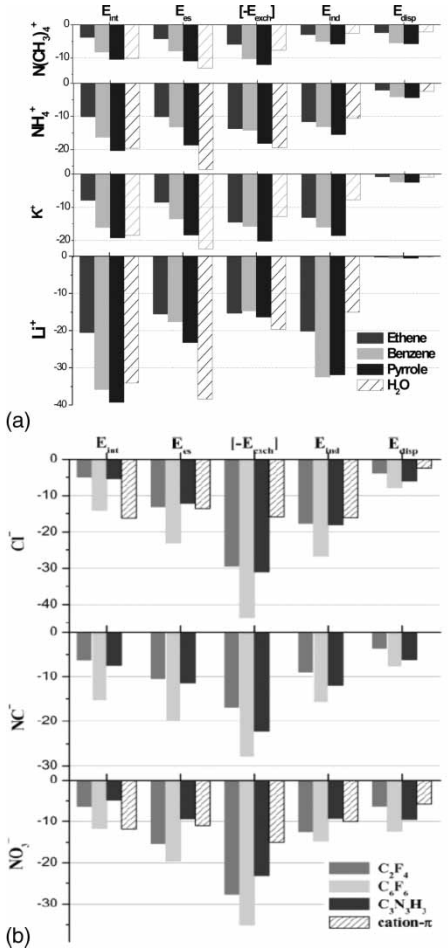

FIGURE 2 a) Comparison of cation–π and cation–water interactions. Notice the distinct differences in various interaction energy components as a result of changes in the nature of the cation and the π-system. b) Comparison of the magnitude of the interaction energy components of Cl^-, NC^-, and NO_3^- complexes with C_2F_4, C_6F_6, and $C_3N_3H_3$. As the cation–π complex corresponding to that of Cl^- with C_6F_6, the data of the K^+–benzene complex are presented, and as the complex corresponding to that of NO_3^- with C_6F_6, the data of the $C(NH_2)_3^+$–benzene complex are plotted.

repulsive exchange energies is more pronounced in the ethene than in the benzene complexes [69]. This leads to a smaller variation in the intermolecular distances in the benzene complexes.

The π–π interactions are one of the most intriguing non-covalent interactions, in the sense that the negatively charged and diffuse electron clouds of the π systems exhibit an attractive interaction. This interaction is dominated by dispersion interactions, when the π 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 [97,98]. The interaction of two benzene rings (benzene dimer) has been widely investigated both experimentally and theoretically. The experimental estimates of the interaction energy are of the order of ~2 kcal/mol [99,100], which indicates that the attraction is appreciable and significantly influences the interaction between phenyl rings in solution or other environments, in addition to other factors such as solvophobic effects. The benzene dimer can manifest itself in T-shaped or parallel-displaced structures. The available evidence seems to indicate that the edge-to-face form is the most stable, but nearly isoenergetic to the parallel displaced form. The isolated benzene dimer is extremely floppy and can coexist in both forms. Although the dispersion energy dominates aromatic interactions, it tends to be almost canceled out by the exchange repulsion. Thus, the subtle difference in stabilization/destabilization by substitution is represented rather by electrostatic energies, while the dispersion energy together with the exchange repulsion augments the electrostatic energy in substituted aromatic systems. In a subsequent section, we take advantage of the fact that the interconversion between different forms or orientations of the two interacting π systems can be exquisitely controlled [101]. In order to have maximum control on this interconversion, we use electrochemically and photochemically active π systems (quinone and hydroquinone) [102].

Interactions Involving Quantum Species

We note that the interactions involving quantum species like single electrons [103–107], photons [108,109], protons [110–113] and paramagnetic atoms [114] are of importance in understanding the modulation of properties by external stimuli. These arise from the photochemical (involving photons), chemical (involving changes in ion and pH concentrations [101]), electrical (involving electrons) and spintronic origins. Intermolecular interactions involving quantum species have implications in nanomaterial design such as responsive sensors, molecular devices, etc.

MANIFESTATIONS

A vast majority of weak intermolecular interactions are reversible. Though the interactions are weak, the additive effect can magnify the effect of very weak individual interactions. This cooperative effect is responsible for the physical characteristics of a vast majority of chemical and biological systems [115]. One of the widely-known manifestations of cooperative effects is self-assembly. With the aid of understanding of 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.

Cation and Anion Ionophores/Receptors

The design of novel ionophores and receptors has potential utility in environmental and biological systems [116–125]. Various receptors showing either cation recognition [126–135] or anion recognition [136–179] have been synthesized and investigated in the past decades. Despite these achievements, further research efforts are required to address the issues related to the selective recognition of anion/cation in real life samples for environmental or biological use. To this end, it is desirable to understand and analyze the conformational changes of receptors upon complexing with a cation/anion. Even though these conformational changes would affect the total free energy of binding due to the loss in entropy of the system, the binding enthalpy is highly correlated with the binding internal energy when the entropy effect is not significant and hence the binding internal energy could be correlated to the experimental binding free energy. In such cases, *ab initio* characterized interaction energies for an ion interacting with diverse receptors are useful. Since we have discussed the interactions of various ions with water molecules (Fig. 1), it is possible to replace the water molecules of the hydrated ion clusters by energetically more favorable organic moieties such as the binding arms of receptor. We have investigated the interaction energies of various ions with diverse synthetic organic receptors.

We begin with discussing the design of systems capable of affecting the selective recognition of the ammonium cation (NH_4^+) relative to the potassium cation (K^+), which is of nearly equivalent size. The first step in the receptor design was an appreciation that the receptors have an optimal space to capture NH_4^+ such that strong interactions with and high selectivity for NH_4^+ could be achieved with cation$-\pi$ interactions. The difference in coordination numbers can be exploited. K^+ favors a coordination number of six, while NH_4^+ favors only four [39,77]. Various benzene based tripodal systems with various binding moieties (pyrazole, dihydro-pyrazole, oxazole, dihydro-oxazole, imidazole, dihydro-imidazole) were investigated [177]. A system with dihydro-imidazole moiety as in **1** (Fig. 3) and N-methyl substituted dihydro-imidazole which shows strong hydrogen bonding had the best selectivity for NH_4^+ over K^+. The π-electron density of the receptor needed to be maximized for the improved binding affinity with cations, though its contribution toward the selectivity was minimal.

An extended concept has been applied to the receptor design for a biologically important molecule, acetylcholine [178]. To have higher affinity and selectivity for acetylcholine over NH_4^+, enhanced dispersion interactions and diminished ionic interactions are utilized. This is done by replacing the imidazole/pyrazole arms of the NH_4^+ receptors by pyrrole as in host **2** (Fig. 3). An attempt to enhance the dispersion interaction by replacing the pyrrole ring with bigger indole ring was made. When the indole rings were skewed while facing toward the center of the benzene ring for the interaction with NMe_4^+, the cation$-\pi$ interaction was diminished. The 1,3,5-tris(pyrrolyl)-benzene showed strong binding affinities for acetylcholine and NMe_4^+, with much better selectivity over NH_4^+ in water. These theoretical inferences were confirmed by experiments. In fact, based on the measurements using ion-selective electrode (ISE) (Fig. 4), system **2** was found to bind acetylcholine selectively over NH_4^+ ($\sim$24 times) at pH 8.0 in buffered solutions.

It would be appealing to explore the possibility of carbon based materials being used as ionophores [179,180]. In an effort to unravel the ion binding characteristics of these materials, we carried out *ab initio* calculations of collarenes (benzene rings linked by methylene linkages), cyclacenes (comprised of only benzene rings) and beltenes (ethene groups linked by methylene linkages) [181] and their complexes with various cations (alkali, alkaline-earth metal and organic cations) in both the gas and aqueous phases (Fig. 3). Both collarenes and beltenes exhibit large binding affinities and high selectivities for metal cations. One of the interesting features of the [n]-beltenes complexing with alkali metal cations was that the change in the selectivity order toward an alkali metal cation was correlated with the changes in the size of the beltene cavity size. In a while, [12]collarene exhibits a pronounced binding selectivity for tetramethylammonium and acetylcholine (Ach). The designed molecules could

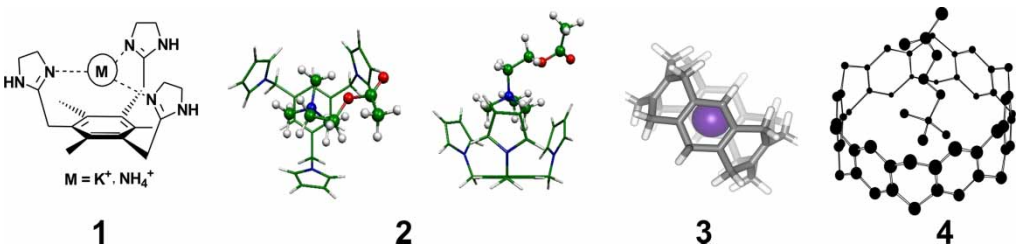

FIGURE 3 Tripodal receptors complexed with NH_4^+ **1** and acetylcholine **2** (top and side view), [8]beltene (**3**) complex with Rb^+ and [12]-Collarene complexed with acetylcholine (**4**).

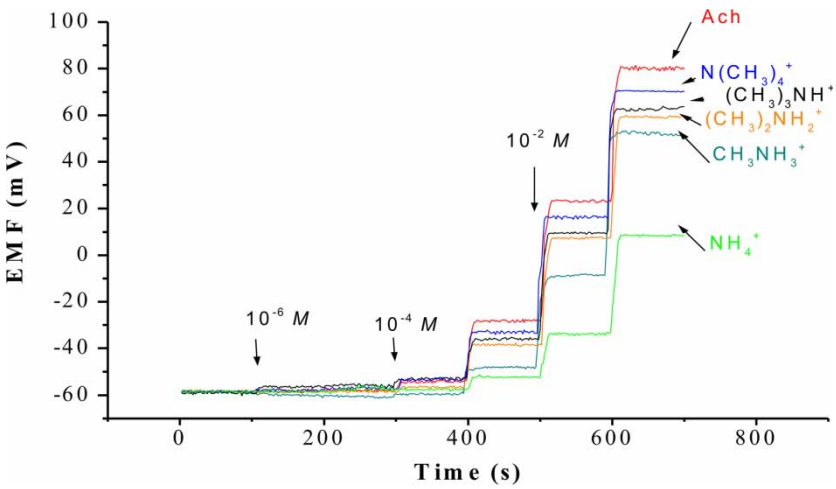

FIGURE 4 Electro-potential graph showing ISE responses of **2** to ACh and NH_4^+ in a pH 8.0 buffer solution at 298 K. (Reproduced with the permission of American Chemical Society [178]).

be modified to be soluble in polar solvents by adding hydrophilic groups on the edges of the molecules.

It is particularly interesting to note that interactions involving anions are very different from those of cations. Since anions are more polarizable and hence more susceptible to polar solvents than cations, the solvent effect is important. Based on *ab initio* calculations, highly selective anionophores have been designed [182–191]. The $(C—H)^+–X^-$ ionic hydrogen bonding involves the dominating charge–charge electrostatic interaction. The $(C—H)^+–X^-$ ionic hydrogen bonding by the imidazolium moieties in the binding arms of a receptor is stronger than the normal hydrogen bonding stabilized by the pyrrole and urea moieties, and so utilization of such ionic hydrogen bonding improves the binding affinity for the anion. Based on this appreciation, we designed and synthesized many imidazolium based receptors for the recognition of wide range of anions. Imidazolium tripodal receptor **5** shows selective binding affinity toward F^- both in acetonitrile and DMSO [182]. The nitro substitution on the imidazolium moiety enhanced the strength of the $(C—H)^+$–anion interaction due to the enhanced dipole–charge interaction, and hence the binding free energy of **6** with chloride was improved by ~1 kcal/mol in DMSO in comparision with the corresponding unsubstituted receptor [183]. The association constant for Cl^- in a 9:1 mixture of acetonitrile-d_3 and DMSO-d_6 was 1.1×10^6 M^{-1}, while in 100% DMSO-d_6 it was 4800 M^{-1} (Table I). The optimized geometry of **6**-Cl^- is shown in Fig. 6.

Fluorescent photoinduced electron transfer (PET) chemosensors (**7** and **8**) for the recognition of pyrophosphate had also been designed and synthesized (Fig. 5) [184–187] in collaboration with Yoon. One of the puzzling issues involving **7**, seen upon complexing with pyrophosphate, was that it showed maximal PET quenching effect, even though there was no chemical shift of the imidazolium C-2 hydrogen in the ^{1}H-NMR spectrum. This stands in contrast to the general observation that the C-2 hydrogen of an imidazolium moiety undergoes a change in chemical shift upon forming a $(C—H)^+–X^-$ ionic hydrogen bond. Our further theoretical investigation predicted insights into the nature of the interaction of **7** and pyrophosphate. In fact, the optimized geometry of **7** with pyrophosphate shows two distinct modes of interactions between the host and guest. In the first mode, one of the imidazolium C-2 hydrogen atoms has been transferred to pyrophosphate. In the second mode the interaction between **7** and pyrophosphate forms a complex where the orientation of the oxygen atoms of pyrophosphate is not properly aligned for maximal H-bonding with the imidazolium C-2 hydrogen atoms (Fig. 6). The interaction mode described in the second case was the ion–pair interaction which is seen in receptors containing ammonium groups [188]. Both the bonding modes show nearly the same binding energy in the gas phase. However, in acetonitrile the ion–pair complex was found to be 4 kcal/mol more stable than the complex formed by proton transfer (Table I). Recently, we have extended our research effort to include a mechanistic study of receptor **9** (trimethyl-[4-(3-methyl-imidazol-1-ium)-butyl]-ammonium substituted at 1,8 anthracene position) for the chemosensing and differentiation of the biologically important phosphates GTP and ATP [189]. Receptor **9** showed a chelation-enhanced fluorescence quenching (CHEQ) effect for GTP, whereas it displayed a chelation-enhanced fluorescence (CHEF) effect for ATP, ADP and AMP (Fig. 7). Therefore, **9** not only differentiated the structurally similar compounds GTP and ATP but also acted as a potential fluorescent chemosensor for GTP in 100% aqueous solution (pH = 7.4, 10 mM HEPES). The mode of interaction of GTP/ATP with

TABLE I Constants for selected hosts

Host	Anion	$K_a(M^{-1})$[a](or K_1, K_2)	$-\Delta G_{expt}$	$-\Delta E^{sol}_{calc}$	$-\Delta G^{scaled}$
5	F^-	21000	7.25	15.82	7.91
		2400	*4.61*	*23.83*	*7.15*
	Cl^-	7600	6.65	14.35	7.17
		1500	*4.33*	*13.56*	*4.07*
	Br^-	4600	6.35	13.77	6.88
6	Cl^-	*4800*	*5.02*	*15.83*	*4.75*
	Br^-	*490*	*3.67*	*13.19*	*3.96*
7	$HP_2PO_7^{3-}$	$\sim 1.01 \times 10^8$	~ 10.91	17.60(11.53)	11.44(7.49)
	$H_2PO_4^-$	$\sim 1.30 \times 10^6$	~ 8.34	12.76	8.29
	F^-	340000	7.54	11.44	7.43
8	$HP_2PO_7^{3-}$	6.76×10^6	9.31	15.81	9.48
	$H_2PO_4^-$	421000	7.67	13.04	7.82
	CH_3COO^-	126000	6.95	11.39	6.84
	F^-	409000	7.65	12.04	7.23
10	F^-	*28900*	*6.03*	*20.30 (20.29)*	*6.39 (6.29)*
	Cl^-	*2030, 2790*	*4.51, 4.70*	*13.74, 19.39*	*4.12, 5.82*
	Br^-	*100, 10700*	*2.73, 5.49*	*10.75, 16.21*	*3.22, 4.86*
12	CH_3COO^-	187000	7.19	15.5	10.1
	F^-	162000	7.10	14.2	9.2

[a]The binding constants of **5** [182], **6** [183], **10** [190] and **12** [191] were calculated from ^{1}H-NMR titrations, while that of **7** [185,187] and **8** [185,187] from fluorescent titrations. Values in italics correspond to DMSO. Anions used are in the form of the tetrabutylammonium salts. Calculations were carried out at the B3LYP/6-31(+)G* level of theory. $\Delta E^{sol}_{calc} = \Delta E^{sol}_{1-anion} - \Delta E^{sol}_{sol-anion} - \Delta E^{sol}_{TBA-anion}$, where $\Delta E^{sol}_{1-anion}$ is the interaction energy of the **1**-anion complex in acetonitrile/DMSO solution based on Isodensity surface polarized continuum model (IPCM), $\Delta E^{sol}_{sol-anion}$ is the interaction energy of the anion with solvent molecules in the first solvation shell of an anion. $\Delta E^{sol}_{TBA-anion}$ (sol = acetonitrile/DMSO) is the interaction energy of tetrabutylammonium with the anion in solution. The countercation correction was applied only to F^-, since this effect is not significant for the other anions [190]. The free energy change (ΔG_{scaled}) was approximately obtained by scaling the internal energy change [30% for DMSO (applied to **10**); 50% for acetonitrile (applied to **5** and **6** and receptors with three or more interaction sites); 65% for acetonitrile (applied to receptors with two interaction sites such as **7**, **8** and **12**)]. This is in concordance with the general trend of the decreasing order in the ratio of free energy to internal energy for the halides upon increasing the number of coordinated water molecules [19,45]. For **7**, the values in parentheses correspond to the first binding mode with $HP_2PO_7^{3-}$ as described in the text. For **10**, the value in parentheses corresponds to the binding energy calculated with the inclusion of one water molecule coordinated from the top.

9 was found to be quite unique, where the nucleic base of GTP/ATP forms a T-shape interaction via strong π−H interaction with the central ring of the anthracene moiety (Fig. 6). The selectivity of GTP is about 6 times that for ATP, and this difference was ascribed to the differences in the strength of the π−H interaction for GTP (π−HN interaction) and ATP (π−HC interaction).

Calix-[4]-imidazolium-[2]-pyridine, **10** [190] showed high selectivity for fluoride anion ($K = 28900\,M^{-1}$ in DMSO-d_6) due to the unique 1:1 binding mode of interaction (Fig. 6), whereas **10** showed the 1:2 binding profile with other halide anions. In the crystal structure of **10** with F^- we noticed that **10** binds the single fluoride anion such that all four $(C—H)^+$ groups of **10** are oriented toward the cavity. This anchors the fluoride anion to the center of the macrocyclic core with the strong ionic hydrogen bonding. We also observed that a water molecule (from the trihydrated tetrabutyl ammonium fluoride salt) was coordinated from the top. Our calculation shows that the presence of one water molecule destabilized the binding free energy by ~ 0.1 kcal/mol. If we compare this interaction mode with the $F^-(H_2O)_5$

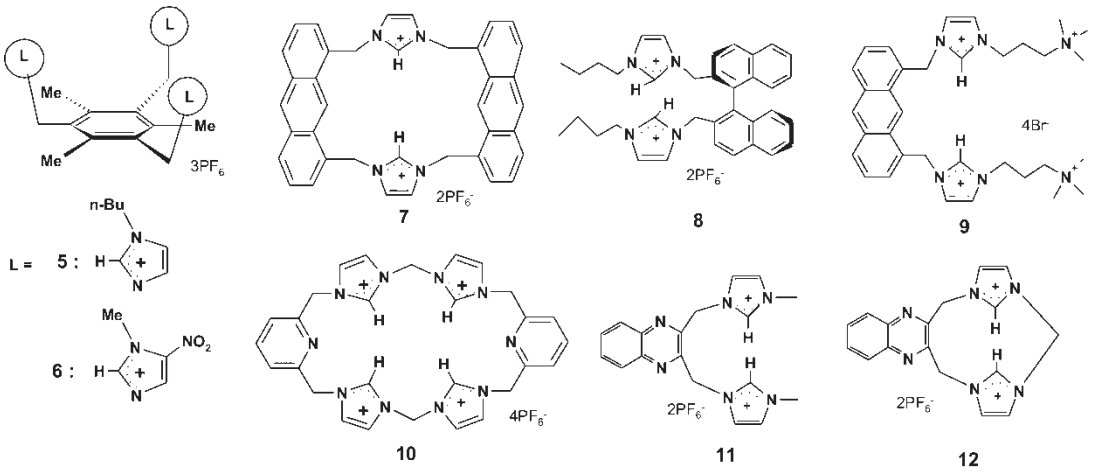

FIGURE 5 Tripodal imidazolium receptors (**5**,**6**), anthracene imidazolium dimer (**7**), binaphthyl based imidazolium receptor (**8**), 1,8-anthracene substituted trimethyl-[4-(3-methyl-imidazol-1-ium)-butyl]-ammonium receptor (**9**), calix[4]imidazium[2]pyridine receptor (**10**), and quinoxaline imidazolium receptors (**11**,**12**).

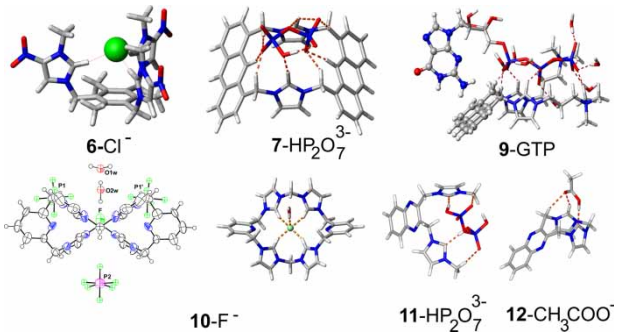

FIGURE 6 Calculated structures of **6**-Cl^-, 7 – $HP_2O_7^{3-}$, **9**-GTP, **10**-F^- (crystal structure is shown in the left side [190]), **11** – $HP_2O_7^{3-}$ and **12**-CH_3COO^- complexes.

cluster structure (Fig. 1), we may say that the four water molecules at the base of the cluster has been replaced by four imidazolium moieties, whereas the top water molecule represents the solvent affect on the binding of F^- to **10**. The imidazolium based quinoxaline receptors **11** and **12** show similar excimer peaks at ~430 nm with various anions except for pyrophosphate and acetate. Upon adding pyrophosphate/acetate to **11**/**12**, deprotonated complexes were formed where hydrogen in the imidazolium was transferred to pyrophosphate/acetate. As a result, rapid charge transfer in excited state was observed from the quinoxaline moiety to the deprotonated imidazolium moiety. As a result, a characteristic charge transfer peak at ~500 nm is observed in the fluorescent spectra of **11**/**12** upon binding with pyrophosphate or acetate, respectively [191].

We have designed various amphi-ionophores with cyclopeptides [192,193]. The concept of binding either an anion or a cation by the conformational changes of the receptor has been experimentally realized [194,195].

Organic Nanotubes

An interesting aspect of self assembling organic nanotubes from non-tubular units of calix-4-hydroquinone (CHQ) [196–198] was that the theoretical design preceded and was done in parallel with the actual synthesis and elucidation of the X-ray structure (Fig. 8). In the absence of water, for each CHQ monomer, the number of dangling H atoms is four, while in the presence of water, these dangling H atoms of CHQs form HQ–(water–HQ–HQ–)$_n$–water chains. As the strength of one-dimensional short H-bonding interaction (~10 kcal/mol) is stronger than the strength of the π–π stacking interaction, the assembling along the 1-D short H-bond relay is much more favorable. In experiments carried out in the presence of water, CHQs assemble to form long tubular structures with four infinitely long short strong H-bond arrays. The CHQ tubes, in turn, form bundles with intertubular π–π stacking interactions, resulting in crystals with well-ordered 2-D arrays of pores. A needle-like nanotube bundle exhibits the infinitely long one-dimensional H-bonding network between hydroxyl groups of CHQs and water molecules along with well-ordered intertubular π–π stacking pairs (Fig. 9).

Organic Nanodevices

The quest for nanodevices implies that one has to induce motion in a system using external or internal means. These include changes in pH, voltage application, laser excitation, irradiation, etc. We discuss one such device (a molecular flipper), which has been designed, synthesized, and characterized [101]. 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 quinone moiety in the molecular system.

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. The stacked conformer is 7 kcal/mol more stable than the edge-to-face conformer in oxidized state,

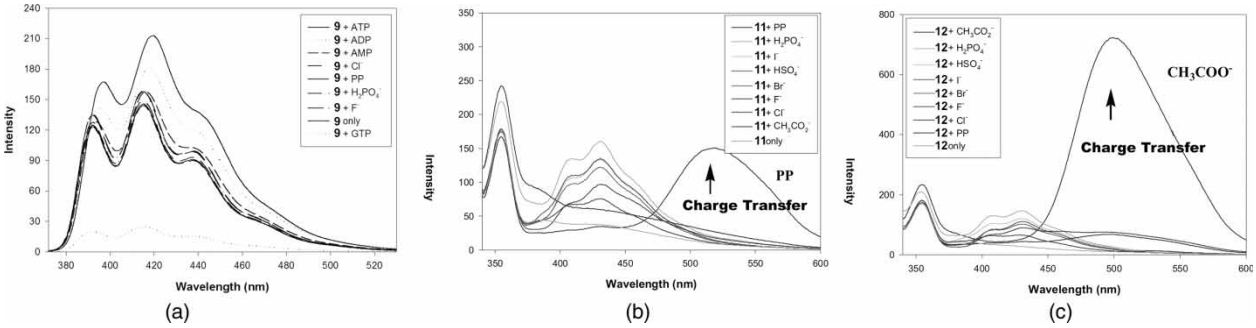

FIGURE 7 a) Fluorescent emission changes of **10** (6 μM) seen upon the addition of the tetrabutylammonium salts of HSO_4^-, Cl^-, F^-, $H_2PO_4^-$, pyrophosphate and the sodium salt of AMP, ADP, ATP, and GTP (300 equiv) at pH 7.4 (50 mM HEPES) (excitation at 367 nm). b) and c) Fluorescent emission changes of **11** and **12** (3 μM) upon the addition of tetrabutylammonium salt of HSO_4^-, $CH_3CO_2^-$, I^-, Br^-, Cl^-, F^-, $H_2PO_4^-$ and $HP_2O_7^{3-}$ (100 eq.) in acetonitrile (excitation at 320 nm, excitation and emission slit: 10 nm).

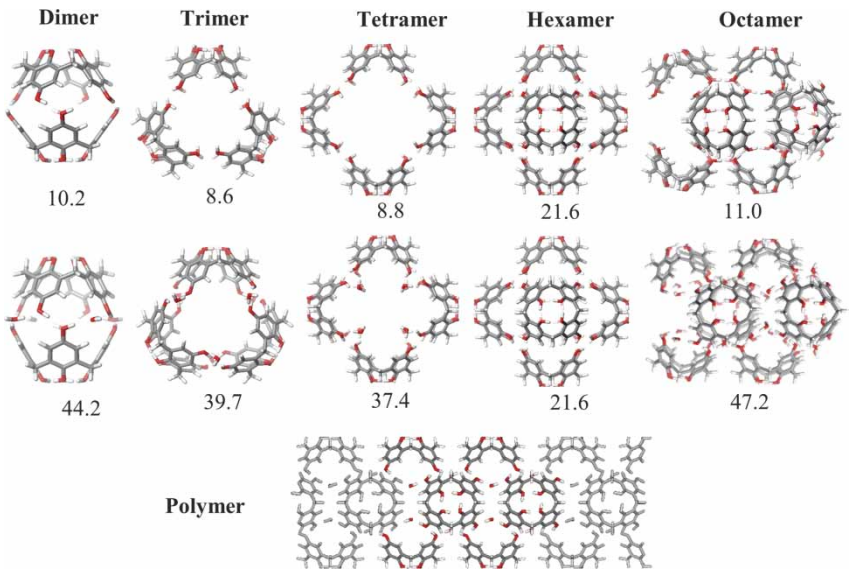

FIGURE 8 Demonstrating self assembly process without (top) and with (below) water molecules: dimer, trimer, tetramer, octahedral hexamer, and tubular octamer as a repeating unit of the tubular polymer of CHQs. Values given below each structures are the calculated binding energy (kcal/mol) at the B3LYP/6-31G* level of theory. It is clearly seen that the presence of water molecules highly stabilizes each system.

whereas the edge-to-face conformer is 9 kcal/mol more stable than the stacked conformer in reduced state. Thus, the subtle control of the conformational characteristics of 2,11-dithio[4,4]metametaquinocyclophane (MQC) and 2,11-dithio[4,4] metametahydroquino-cyclophane (MHQC) by electrochemical and/or photochemical means leads to a very interesting model of a potential molecular device. The cyclic voltammograms of MQC exhibits two reversible redox reactions (Fig. 6). In aprotic media, quinones exhibit two reduction peaks separated by 0.7 V, which corresponds to the formation of a radical anion species and a dianion species of quinones, 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 quinone moiety.

Thus, a cyclophane system composed of quinone and benzene rings exhibits a flapping motion involving squeezing and thrusting motions in the presence of solvent molecules by electrochemical redox process (Fig. 10). This case illustrates a promising pathway for harnessing the differences in the relative magnitudes of different kinds of intermolecular interactions to design a mobile nanomechanical device for drug delivery and nanosurgery.

CONCLUSION

In this mini-review, we have illustrated our efforts to understand the principles of molecular interactions and their application to the design and investigation of ionophores, molecular assembly, and molecular

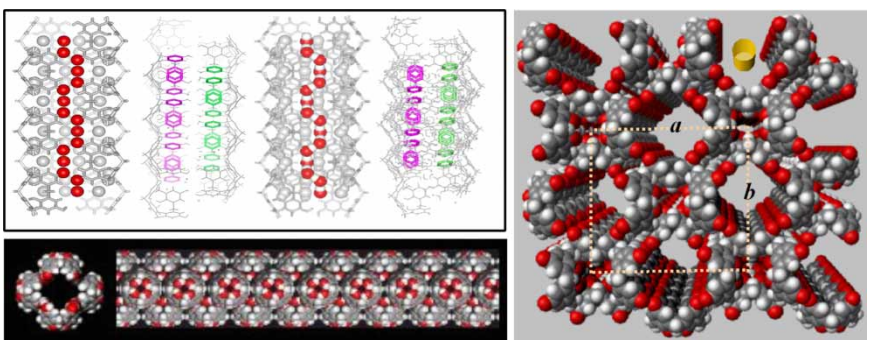

FIGURE 9 Calix[4]hydroquinone nanotubes showing the longitudinal one-dimensional H-bond relay vs. intertubular $\pi-\pi$ stacking competition phenomenon in the assembling process. Each tube has four thin threads of infinitely long one dimensional hydrogen bond relays, and the diameter of each is 8 Å. The unit cell in the X-ray structure is drawn by the dashed lines. (Reproduced by permission of American Chemical Society [196,198].)

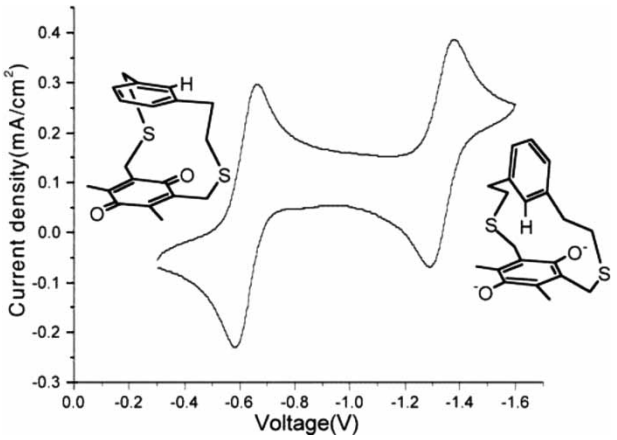

FIGURE 10 Cyclic voltammogram of MQC(left)/MHQC(right) (1 mM) in acetonitrile with tetrabutylammonium dihydrogen phosphate (0.1 M) at 25°C (scan rate 100 mV/s). (Reproduced by permission of American Chemical Society [101].)

devices. The progress we have made is illustrated by a wide variety of examples. Quantitative estimates of the magnitudes of various intermolecular interactions and energy components are very useful in determining their relative importance. However, weak interactions are very important in the sense that they steer and promote much stronger interactions. Given the success of our approach in designing experimentally viable ionophores and self-assembled molecular systems and devices, we believe that the coming years will see the use of these and other nano-recognition approaches in the development of diverse supramolecular systems and nanomaterials.

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