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Computational Approaches in Molecular Recognition, Self-assembly, Electron Transport, and Surface Chemistry

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As computational methods have been drastically developed in parallel with the advancement of the computer and electronics industry, computational chemistry now shows a wide number of applications for many complicated supramolecular systems which were not feasible to carry out in the past. In many supramolecular systems, their structures and functions have been successfully understood with the aid of computational approaches. In this mini-review, several computational approaches will be introduced that have been applied to molecular recognition, self-assembly, photo-induced electron transfer, and chemical structures and reactions on surfaces as well as basic computational methods.

Keywords: Molecular recognition; Self-assembly; Electron transport; Surface; Density functional theory; *Ab initio* calculations

INTRODUCTION

Supramolecular chemistry is in the central part of the bottom-up approaches to nanoscience and nanotechnology. This branch of science is highly interdisciplinary and is mostly concerned with advancing structural complexity such as molecular recognition [1,2], molecular engineering [3–5], and self-assembly [6–9]. The most frequently utilized intermolecular interactions are non-covalent weak interactions such as the hydrogen bonding, π – π stacking, metal-ligand coordination, van der Waals forces, hydrophobic, ionic, and other weak interactions. Supramolecular chemistry is often pursued to develop new functions that cannot appear for a single molecule. These functions include magnetic properties [10–12], light responsiveness [13–16], catalytic activity [17–19], self-healing polymers [20], chemical

sensors [21–23], etc. These basic functional features may be translated into structural features. The modification of chemical properties of porous coordination compounds including polymers is currently a big challenge in the field of material chemistry [24–26]. Until now, many supramolecular families with porous networks functioning as molecular adsorbents for hydrogen [27], nitrogen [28–30], metals [31–33], etc, have been synthesized. They have been successfully designed based on their existing experiences and chemical intuitions. In general, to understand molecular growing or molecular functioning mechanisms at the molecular or atomic level is very difficult. Computational study can contribute to the molecular or atomic level understanding of the structural and thermodynamical features involved in the process of molecular recognition and supramolecular organization. In addition, computational application can be expanded to automation, simulation of processes, visualization, etc. However, computational approach only is impossible to fully understand the supramolecular systems without experimental assistance. In this regard, collaborative studies by both computational and experimental groups are highly encouraged in the supramolecular chemistry.

Essentially, common features of all of the supramolecular systems are non-covalent interactions, which provide the clips linking the building blocks, leading to well organized superstructures. Thus, many theoretical studies have been focused on the origin of various intermolecular interactions [34–39]. The synthetic systems are generally well organized and defined, and well characterized in terms of their structures in the solid state and

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in solution. Thus, they are particularly suitable for computational approaches. In the past, it was impossible to deal with large supramolecules using computational quantum mechanical methods. During the recent past, the computational capacity has been growing exponentially, with the advancement of computer industry, and now we can deal with large and complicated molecular systems quantum mechanically. Nowadays, computational approaches have been successfully applied to a number of supramolecular systems [40–49]. When we know X-ray crystal structure, we can compare it with the computationally obtained structure. Then, if the structures are quite similar, the computational analysis may give the basic mechanism at the molecular level for the photo-induced fluorescence, color changes, etc., when the supramolecule senses guest molecules [50–63]. Even if we do not know definite crystal structures, the computational results aid to analyze the structures and visualize the important intermolecular interactions involved. In this short review, we will present recent examples for the computational approaches to supramolecular chemistry as well as basic computational methods.

COMPUTATIONAL METHODS

The main interaction forces governing the formation of supramolecules are weak intermolecular interactions such as π – π stacking and π –H interactions as well as hydrogen bonding. Thus, to understand the supramolecular structures and functions, these interactions need to be described properly. To this end the electron correlation effect should be included. However, such calculations are very limited to relatively small molecular systems where quite accurate calculations such as MP2, CCSD, and CISD can be used. However, in very large supramolecular systems, molecular mechanics (MM), semiempirical, *ab initio* HF calculations as well as molecular dynamics and Monte Carlo simulations have often been used. Very excitingly, density functional theory (DFT) calculations treat electron correlation effect by using parameterized functionals at low cost (its computing time is similar to that of HF, while HF calculation does not deal with the electron correlation effect). Though, DFT calculation has been criticized due to insufficient description of π – π stacking and van der Waals interactions [64–66], it has been widely used for large molecular systems [67,68].

Most quantum mechanical (QM) calculations are for the gas phase behavior. Lessons from studies of the crystalline state have greatly influenced the development of models for intra- and inter-molecular interactions in condensed phases. The important contributions of Allinger on hydrocarbons and their derivatives [69] showed that MM can be a reliable

and inexpensive tool for conformational analysis in chemistry. Molecular recognition is in essence a dynamical process and requires dynamical and statistical information to characterize the representative structure of flexible molecules. This can be achieved by Monte Carlo (MC) techniques [70–72] or by molecular dynamics simulations. Classical molecular dynamics simulates flexible supermolecules in the gas phase or in solution, and it can explore conformational space accessible up to nanosecond timescale with present computational capacity. In 1998, the world record longest molecular dynamics simulation was reported up to microsecond at that time [73]. However, it is still very time consuming and inapplicable to most real dynamics.

Many supramolecules have been synthesized in solution, and often they finally lead to crystal frameworks. Therefore, the solvent action needs to be implemented in calculations for a certain purpose by one way or another. To date, the most widely used treatment for the solvent effect has been the simple dielectric continuum model [74–76]. However, such a treatment fails to account for the detailed molecular nature of the solvent. The explicit incorporation of model solvent molecules surrounding a solute molecule can provide in principle an accurate means for considering such solvent effects by molecular dynamics (MD) and MC techniques [70–72]. However, such techniques demand a lot of computational cost, and the results severely depend on the potential functions employed. Unfortunately, there have been known only limited well known potential functions, for example, TIP4P and SPC/E potential parameters for water [77–82] and some potential parameters for benzene [83–85], etc. For biological systems including protein which is also considered as a supramolecular family in some sense, we have well known CHARM [86] and AMBER [87–89] potential. Another very efficient way to include the solvent effect is the so-called reference interaction site model (RISM) integral equations, which was derived by Chandler and Anderson [90] and extended by Hirata and Rossky [91–94]. The RISM integral equation has been successfully applied to many liquids and polar solvent systems [95–97]. The extended RISM formalism includes the direct site-site interactions of solute-solvent and solvent-solvent as well as it gives a tremendous computational efficiency. However, even in RISM formalism, we can not avoid some problem to describe the molecular property of the solute in solution when the solute itself bears quantum mechanical nature. Accordingly, there are a lot of studies so-called QM/MM which adapts quantum mechanical treatment of a solute and classical treatment of solvent molecules [98–103]. However, this method no doubt demands a lot of computational cost, and is limited to its applications. During the last decade, a new theoretical method, RISM-SCF has

been proposed, developed, and successfully applied to calculate the molecular properties of a solute in solutions [104–106]. This method is basically an *ab initio* method combining with the RISM formalism in the statistical mechanics of the molecular liquids. The advantage of RISM-SCF method is not only to save computational cost, but also to maintain the molecular quantum mechanical nature of the solute molecule keeping the local solute-solvent site-site interactions such as hydrogen bonding. The quantum mechanical level of theory to describe the solute molecule can be properly chosen [107–115].

As described above, there are a number of computational methods available. Therefore, the calculational methods should be carefully and properly chosen to apply for the understanding of supramolecular structures, energetics, and functions.

MOLECULAR RECOGNITION

Molecular recognition is obviously in the central part of the supramolecular chemistry because functional systems (host or receptor) should be created, modified, and fine-tuned in nature through non-covalent forces to recognize a certain target (guest) molecule. Molecular recognition implies strong and specific binding. To achieve such recognition, a concerted interplay between many sites is the only way, because the interaction of each site is usually weak as shown in Fig. 1. Another requirement for multi-site binding is complementarity between binding sites of host and guest molecules. In other words, complexation will be most efficient when the shapes and arrangement of binding sites in host and guest molecules fit each other. For example, a very large binding energy of -76 kJ/mol for a biotin guest molecule and streptavidin host protein resulted from simultaneous action of more than 10 weak pairwise van der Waals, electrostatic, hydrogen bonding, and some lipophilic interactions [116–118]. Needless to mention, hydrogen bonding has played the central role to the intra- and inter-molecular phenomena

in nature [119]. Basically, we detect the recognition from the change of chemical or physical properties of the host (or receptor) molecule when it recognizes (binds) a guest molecule compared with its own properties.

On account of its simplicity and high sensitivity, fluorescence is becoming of increasing importance for chemical trace detection. The linkage of cation crown ethers with fluorescent dyes [120] provides a novel method for monitoring low concentrations of alkali and alkaline earth metals, and, in this connection, considerable efforts have been devoted to developing fluorescent chemosensors for cations and neutral guests [121–123]. These photophysical properties can be understood from the time resolved spectroscopy [124–127]. However, in many cases, such experiments are inapplicable, in which molecular orbital calculations can be an alternative tool. Recently, a computational study was reported to understand the on-off switch behavior of calix[4]-crown chemosensor [128]. The synthesized fluorescent chemosensor with two different cation binding sites, crown ether on the upper rim and amide with pyrene pendant on the lower rims of 1,3-alternate calix[4]arene (**1**) (Scheme 1), showed an interesting excimer switching behavior. **1** shows an excimer emission peak at around 470 nm which is attributed to two facing pyrene units in an intramolecular π - π stacking arrangement under UV irradiation. Upon the addition of Pb^{2+} solution, the excimer peak was quenched, and it revived under the addition of K^+ solution to the Pb^{2+} solution. The DFT calculations with Becke-3-Lee-Yang-Parr (B3LYP) exchange correlation functionals revealed that the excimer emission band of **1** was mainly attributed to the *dynamic excimer* [129,130] which comes from the excited dimer formed between an excited pyrene (Py^*) and a ground state pyrene (Py), rather than the stable dimer between two ground state pyrenes (Py and Py) which is called *static excimer* [129,130]. This conclusion should be carefully drawn from the reasonable ground state

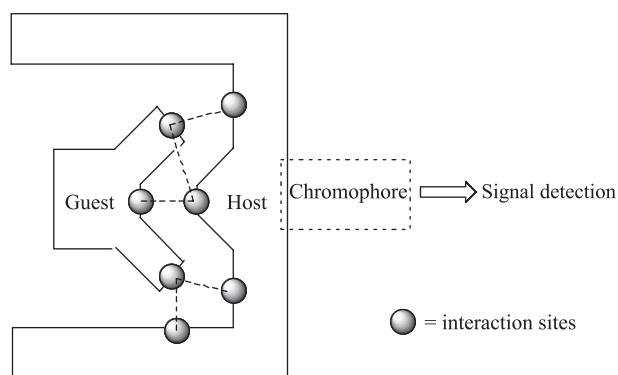
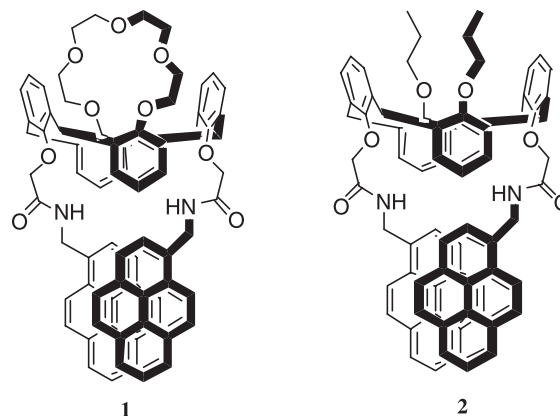


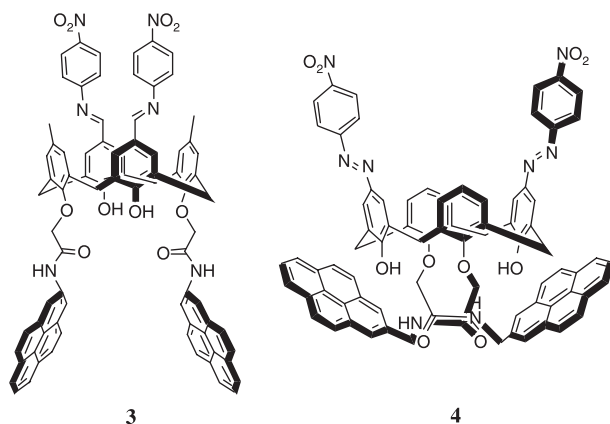
FIGURE 1 Schematic representation of molecular recognition and signaling.



SCHEME 1

structures. When the two fluorophores (pyrenes in our study) do not show a stacked dimer, we could carefully say it may form a stable dimer after irradiation, in other words, after one of the fluorophore is excited, hence it may form *dynamic excimer*. Importantly, in addition to the ground state structure, the frontier molecular orbitals (high lying occupied molecular orbitals such as HOMO and HOMO-1 and low lying unoccupied molecular orbitals such as LUMO, LUMO + 1, LUMO + 2, etc.) can give other informations about the sensing mechanism by fluorescence. Shapes of occupied molecular orbitals (OMOs) give some information about the positions at which the electrons are mainly located, while unoccupied molecular orbitals (UMOs) give some information about the position of holes. Thus, when a light with wavelength corresponding to OMO-UMO energy difference irradiates the molecule, the strong electron-hole interaction can be notified. From such an investigation, we could carefully conclude that the excited dimer can be formed upon UV irradiation which gives excimer emission band. Based on such a rationale, recently synthesized calixarene-based fluorescent chemosensor (**2**) was concluded from the computational and experimental study that **2** shows a *dynamic excimer* band at around 482 nm. However, complexation of F^- by **2** causes a blue shift of the excimer band to 470 nm ($\Delta\lambda = 12$ nm) and a red shift of its absorption band ($\Delta\lambda = 54$ nm). This blue-shifted excimer emission was attributed to a pyrene dimer formed in the ground state, a so-called *static excimer*.

Calix[4]arenes have a high selectivity and binding efficiency for both cations and anions [131–133]. Furthermore, calixarene-based chromogenic sensors have attracted attention due to their ability to visually detect analytes [134]. Most chemosensors developed to date function either by a marked change of fluorescence or marked change of absorption. Previous studies revealed that the excimer band of pyrene pendant in the calix[4]arene family can be a fluorescent fluoride chemosensor [134]. It was also noted that the nitrophenylazo moieties on the upper rim of the calix[4]-crown had a chromogenic role [135]. Kim and co-workers designed chromogenic and fluorescent chemosensors and synthesized calix-luminophores (**3** and **4**) bearing both pyrene pendants with amide linkages and 4-nitrophenylazo group (Scheme 2) [136]. *Ab initio* calculations for the complexation of **3** and **4** with F^- revealed that a fluoride anion binds the amide protons of **3**, while it binds the hydroxy protons of **4**, which was consistent with the experimental analysis. The experimentally observed spectroscopic data was also qualitatively explained from the calculated structures and electronic properties. The highest occupied molecular orbitals



SCHEME 2

(HOMOs) of **3**, **4**, $3\cdot F^-$, and $4\cdot F^-$ explained the difference of UV spectra changes, hence color changes of **3** and **4** upon the addition of F^- . It was also concluded that the reason of having similar UV spectra in **3** and $3\cdot F^-$ is due to the methylene spacer between $-NH$ and pyrene which does not allow the resonance when the amide proton is deprotonated by the added F^- . On the other hand, **4** and $4\cdot F^-$ reveal the significantly different UV spectra due to resonance effects.

Mukamel and co-workers have developed a very useful algorithm, what is called collective electronic oscillator (CEO) algorithm [137–139] to understand electronic transitions of molecules [140–151]. Normal mode analysis gives us understanding of fundamental vibrational transitions. In other words, it explains an experimental vibrational (IR or Raman) spectral peak originates from a certain collective atomic motions. For example, a certain vibration is composed of 60% C=C stretching, 30% C–C stretching, and 10% H–C–C bending motions. Similarly, CEO calculation gives us what kinds of electronic motions are involved for the electronic spectra, that is, UV spectra. CEO calculation was applied to understand fluoride chemosensors based on naphthalene (**5**). In Fig. 2(b), the simulated UV spectra of **5**, its deprotonated form (5^-), and its complex with fluoride ($5F^-$) were shown with the CEO algorithm using the lowest 50 oscillators. The origin of each absorption peak can be understood from the transition densities as described in our previous work [152]. As an example, the transition density contour for the lowest energy peak of $5F^-$, denoted as A1($5F^-$), was represented in Fig. 2(c). (Refer to reference [152] for atomic numbering) The transition densities represent the dominating electronic oscillators corresponding to A1($5F^-$) absorption peak. The diagonal elements give the atomic charges, while the off-diagonal elements represent the electron-hole coherences. For example, the density value at (10,15) position of (x, y) represents the how strongly the electrons of atomic

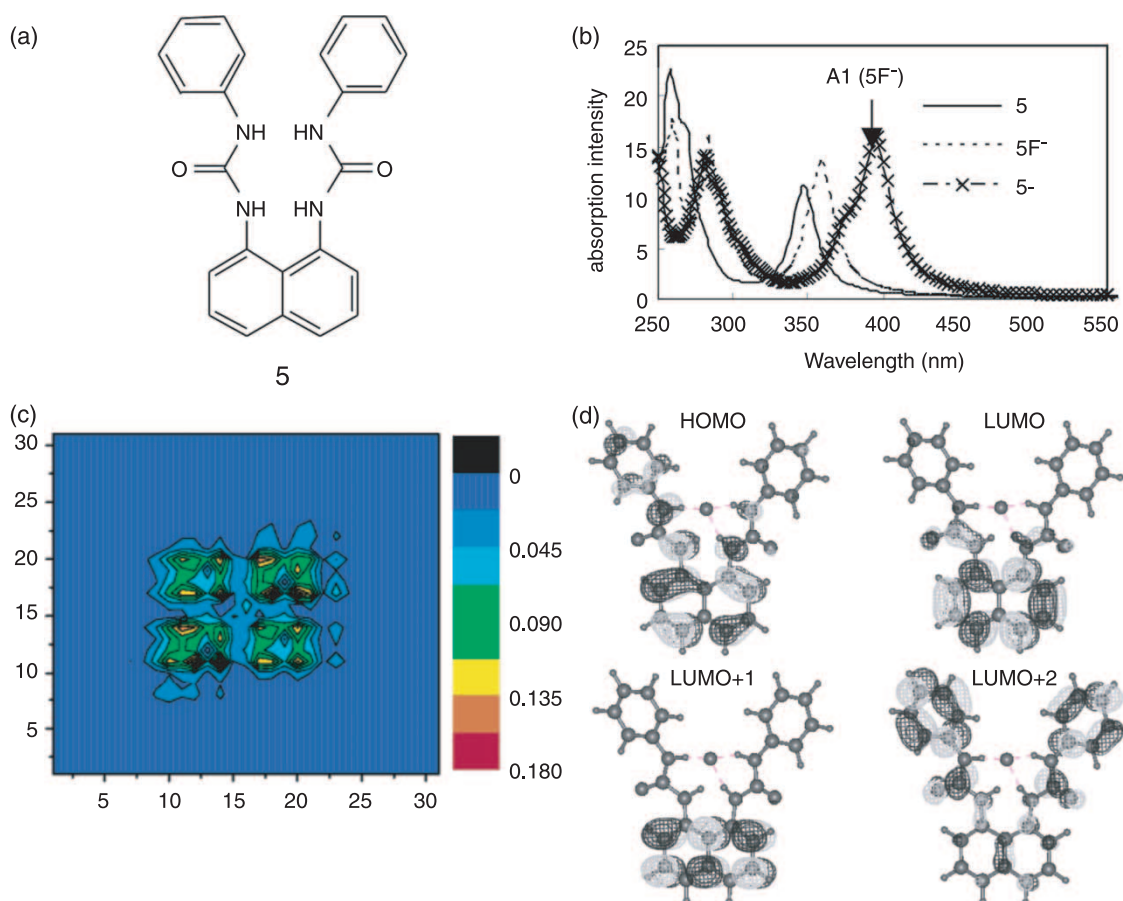


FIGURE 2 Schematic representation of **5** (a), simulated absorption spectra of **5**, $5F^-$, and 5^- (b), transition density contour for $A1(5F^-)$ peak (c), and frontier molecular orbitals (d) of $5F^-$.

site 10 are interacting with the holes of atomic site 15. In the point of molecular orbital picture, it represents the interactions between occupied molecular orbitals at 10 and unoccupied molecular orbitals at 15. HOMO and low lying unoccupied molecular orbitals were shown in Fig. 2(d) for comparison, and the MOs are consistent with the transition density analysis except that the ordering of LUMO and LUMO + 1 is changed. As a matter of fact, MO calculations are basically very good for ground state properties, and the occupied MOs are well described. However, the orbital energy ordering for unoccupied MOs are often not properly obtained. Combining the UV spectra, transition density contours, and molecular orbital shapes, each UV spectral peaks can be clearly understood as shown in the previous study. NMR shielding tensor obtained by *ab initio* calculations is another useful information to compare with experimental observations. As an example, refer to the reference [152]. Usually, NMR shielding tensors were computed with the Gauge-Independent Atomic Orbital (GIAO) method [153–156]. Currently available functionals do not include a magnetic field dependence, so DFT methods do not provide systematically better NMR results than HF [157].

Computational study also aids to understand the binding site when there are more than two possible binding sites [152]. A recent computational study was successful to explain the binding features of a functionalized inorganic nanotube for selective detection of Cu^{2+} and its color changes upon the Cu^{2+} recognition [158].

SELF-ASSEMBLY

One of the goals in supramolecular chemistry is to design and synthesize functional frameworks for certain specific purposes. First of all, it is very attractive to design fantastic super-structured materials starting from simple molecular building blocks. This phenomenon is called self-assembly or self-aggregation. The monomeric building block is not always a growing unit; dimer or trimer can be a growing unit as seen in Fig. 3. In many cases, monomers associate to form a certain size of clusters by hydrogen bonding or other weak interactions at first, then they stack to finally give superstructured networks. Furthermore, self-assembly sometimes takes place thermodynamically [159,160] and kinetically [161–163] sometimes.

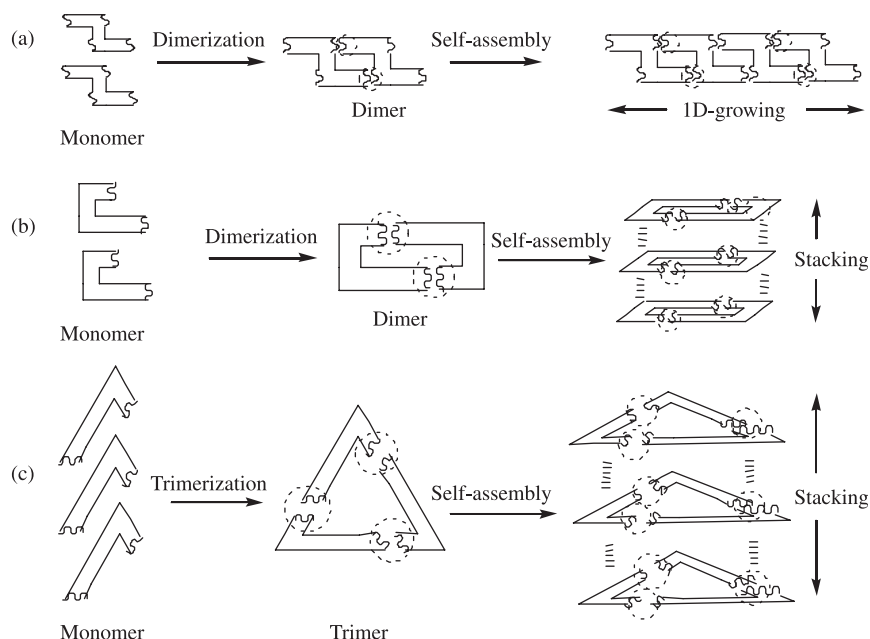


FIGURE 3 Schematic representation of self-assembly growing from monomeric (a), dimeric (b), and trimeric (c) growing units from monomeric building blocks.

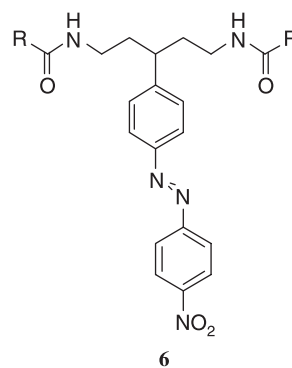
These make it difficult for computational chemists to solve the self-assembly problems. For thermodynamic problems, we have only to figure out the energetics for all the probable structures step-by-step. However, for the kinetic problem, we have to think about all the possible reaction pathways for each step (monomer to dimer, dimer to tetramer, tetramer to octamer, etc.), and all these steps heavily depend on the experimental conditions. Thus, it is absolutely impossible to investigate self-assembly problem by QM calculations. In spite of such difficulty, computer-aided molecular design based on fragment model studies has been used to compare with experimental results [164–168].

At this stage, it is very interesting to think about a question about “How do the molecules assemble together?” It is quite general to consider that all the molecules are the same, and any two molecules are non-interacting at distant configurations. Then, the molecules could move freely except that they are close enough to feel some interactions between them. Thus, this process can be treated by translation and rotation without any interactions until they come together closely.

With this idea, we recently tried to understand self-assembled structures and to investigate existing intermolecular interactions of *p*-nitro-azobenzene-coupled bis-alanine (**6**) (Scheme 3). In experiment, when D-alanine/L-alanine with long alkyl chain was used as R group, right-handed/left-handed nanohelical string was obtained as “Gel” state in most organic solvents [169]. However, when long alkyl chain was not used as R group, “Sol” marks were obtained regardless of the existence of alanine group. When a long alkyl chain was used without alanine

moiety as R group, almost equal amount of “Gel” and “Sol” marks were obtained. Apparently, both long alkyl chain and alanine moiety play a crucial role to form a “Gel” state. For the *ab initio* calculations, the long alkyl chain was replaced by methyl as usual. First, the monomer structure was optimized. Then, the monomer was replicated towards a reasonably assembled dimer structure after many trials by translation and rotation of the replicated monomer with the original monomer fixed. Similarly, the dimer can be replicated to form a reasonable aggregated tetramer. Figure 4 shows the dimer, tetramer, and octamer generated in such a fashion.

It should be mentioned that any kind of interaction energies were not considered between monomers, between dimers, and between tetramers, etc. Without consideration of such intermolecular interactions, it is very interesting to note that the dimer showed perfect hydrogen bondings network between amide



SCHEME 3

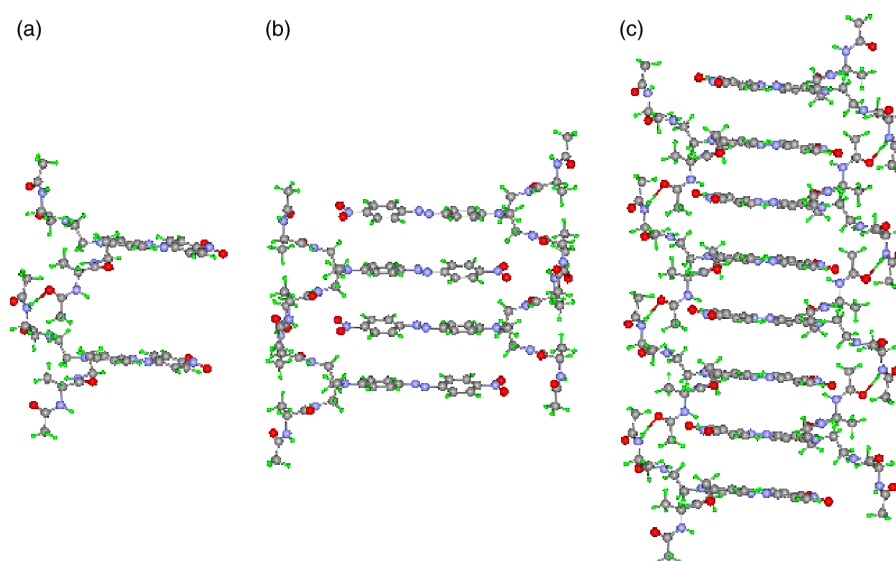


FIGURE 4 Virtually assembled structures of dimer (a), tetramer (b), and octamer (c) of **6** with $R = \text{CH}_3\text{CONHCH}(\text{CH}_3)\text{CH}_2$.

functional groups of the alanine group as seen in Fig. 4. In reality, they obviously feel intermolecular forces each other as they approach, and better fit for their association with structural changes. In addition, the tetramer shows stacked geometry with interplanar distance of $\sim 4.6 \text{ \AA}$. However, typical inter planar distance of π - π stacking interactions is around 3.5 \AA . Longer interplanar distance is probably due to the ignorance of intermolecular interactions. The interplanar distance should be reduced if the tetramer geometry was fully optimized by *ab initio* calculation. The structures with long alkyl chains may be deduced from these assembled structures where methyl groups were used for simplicity in the calculations. It can be grasped that the alkyl chain-alkyl chain interaction have van der Waals interactions which can be named as hydrophobic interactions in solution. Thus, from the computational results, it can be concluded the self-assembly growing process may happen as followings: At first, the monomers move by diffusion, and as they come closer they assemble by hydrophobic interactions. At this point, they may not feel the hydrogen bonding interaction because they are still in random motion, and they are in semi-rigid structure by hydrophobic interactions. Then, the dimer structure can be rigidly clipped when they have an orientation to feel hydrogen bonding interactions. This analysis is consistent with the experimental results that "Sol" marks were obtained regardless of the existence of alanine group when a long alkylchain was not used as an R group, implying the importance of hydrophobic interactions. This computational approach has been applied successfully to study the self-assembled structures of alanine-functionalized porphyrin derivatives [170]. This approach is very much related to the previous experimental design of supramolecules based on molecular building block (MBB) approach [171–175].

ELECTRON TRANSPORT

One of the most fascinating research areas is molecular electronics, which involves the use of single or small packets of molecules as the fundamental units for computing [176–185]. The basic units of an electronic device are the diode and the transistor. These basic units can be realized by introducing a molecular wire and electron confinement [186–189]. Electron confinement is often treated with nonconjugated functional groups such as methylene, while molecular wires usually contain π -electron conjugated systems [190–193]. Recently, we have studied the charge transfer within a molecule or between molecules [194] and found a simple expression to quantify the amount of intramolecular charge transfer in the donor- π -conjugated bridge-acceptor systems [195]. We also studied the effect of solvent on the intermolecular charge transfer between the donor molecule and the acceptor molecule [196]. The possibility that the π -stacked base pairs of DNA might serve as a pathway for charge transfer was advanced over 30 years ago [197,198]. However, because of synthetic difficulties, examples of π -stacked molecules with multiple layers were scarce. Recently, Rathore *et al.* synthesized a versatile class of π -stacked polyfluorenes [199]. In polyfluorenes, the van der Waals contact between the cofacially oriented fluorene moieties allows effective electronic coupling among them. To provide a fundamental understanding that may prove to be relevant to the electron transport property observed in DNA through π -stacked bases, the families of polyfluorenes are good model compounds to be theoretically investigated. With this motivation, recently we studied the structures, NMR spectra, absorption spectra, and electron-hole interactions in the presence of excitation

light based on *ab initio* calculations and the collective electronic oscillator method. The vertical detachment energy is linearly proportional to the ionization potential, which was reported to be inversely proportional to size in the previous experiment. On the contrary, the electron attachment energy decreases exponentially as size increases, which implies that the electron transport would be possible even for long chains such as F3 and F4. An evidence for the possible electron transport was also noted from the frontier molecular orbitals, as seen from LUMOs of F3 and F4 in Fig. 5. The syn conformers are much more favorable for electron transport through the π -stacked fluorine moieties, and electron transport in DNA may be facilitated through the π -stacked domains. The transition densities obtained by CEO method help assign the absorption peaks as explained in the previous section [128]. For example, the absorption peak around 311 nm was assigned to the electron-hole interactions between electrons in one benzene group and holes in the other benzene group in the same fluorine moieties, and the electron-hole interactions between neighboring fluorene moieties are negligible.

Computational study can be applied to a chemical problem which is experimentally very difficult. Let us describe such an example. Recently, a novel fullerene-porphyrin-fullerene triad, (C₆₀CHCOO)₂-Sn(IV) porphyrin, linked by metal axial coordination was synthesized and the crystal structure was obtained [200]. We carried out DFT calculations to look into the molecular orbitals at the beginning [201]. By mistake as it sometimes happens in experiment, the calculated structure was cis-conformer, while the trans-conformer was obtained in

experiment. After calculation for the trans-conformer, we found that the cis conformer is slightly more stable than the trans one by 1.38 kcal/mol. What is disappointing is sometimes very interesting. Then, we thought about a question, "How does the stability change if an electron is added?" To answer this question, an *ab initio* calculation was carried out and found that the relative stability of the cis conformer is more stable than the trans conformer by 3.29 kcal/mol upon the addition of an electron to the triad. As discussed earlier, the most stable conformer is not always obtained in crystallization experiment if the energy difference is not that large. As a matter of fact, the trans conformer (1.38 kcal/mol higher than cis) was obtained for a neutral triad. When the triad is reduced by one electron addition, the energy difference increased more than twice for the anion triad, thus, it may be possible to obtain a cis conformer. If the cis and trans conformers show different electronic or optical properties, and the two conformers can be reversible to be controlled by oxidation/reduction, the triad system could be a potential candidate for an electrochemical machinery or electrochemical switching device as shown in Fig. 6. From the investigation of frontier molecular orbitals, it was found that electrons are localized in LUMO of only *syn*-fullerene for the cis conformer. On the contrary, for the trans conformer, electrons are localized in LUMO of one of the two fullerene moieties, and the electrons are localized in LUMO2 of the other fullerene moiety, but the LUMO and LUMO2 have the same orbital energy. Thus, the photoinduced electron transfer (PET) may take place unidirectionally in the cis conformer from the

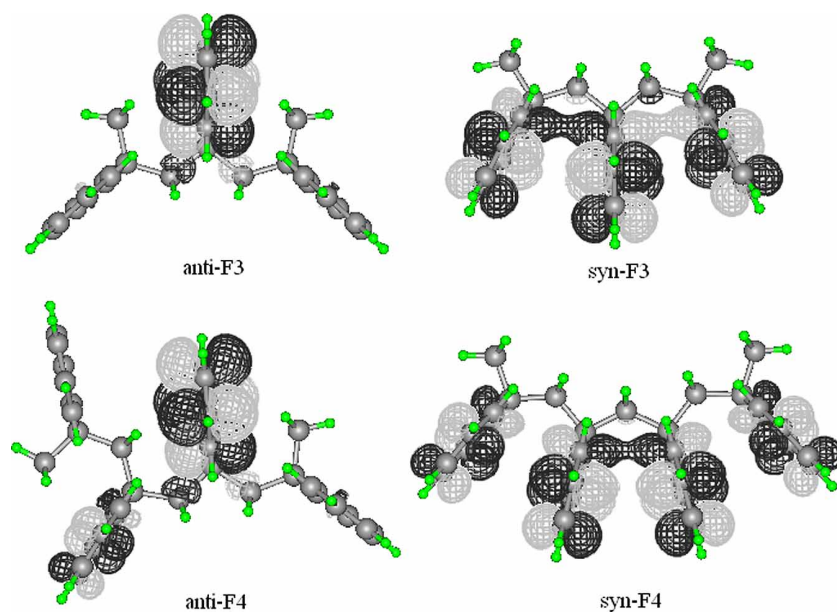


FIGURE 5 LUMOs of anti and syn conformers of F3 and F4.

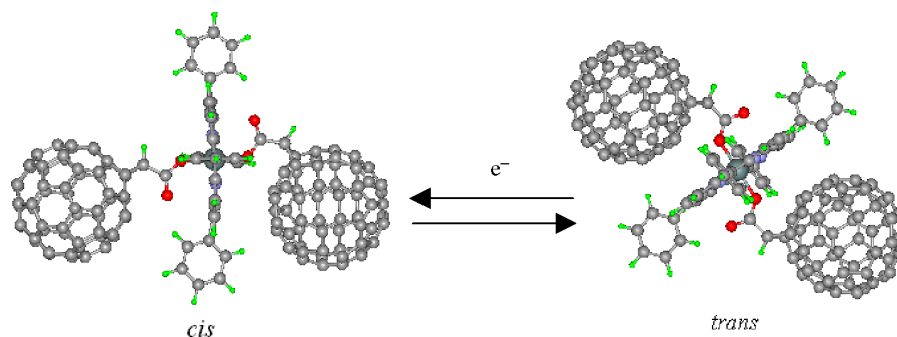


FIGURE 6 Suggested cis-trans conformational change under redox reaction of the fullerene-porphyrin-fullerene triad.

porphyrin to the *syn*-fullerene, while it is bidirectional from the porphyrin to both of the fullerene moieties.

SUPRAMOLECULAR CHEMISTRY ON SURFACE

In recent years, chemical reactions on surface and self-assembled 1D molecular wire on silicon surface have attracted much attention from both fundamental and applied points of view. Essentially, the functional molecules need to be fabricated into a solid state, and the surface science plays a very important role. Fabrication of hybrid organic molecular silicon surfaces has been a fascinating subject because of its potential application for new sensor and molecular device technologies [202–206]. In this section, we will introduce several computational approaches to self-assembled structure and chemical reactions on surface. Choi and Cho studied 1D self-assembled borine wire on Si(001) surface by density functional theory calculations [207]. They found that the self-assembled borine wire undergoes a Peierls instability, giving rise to a periodic structural distortion, a band-gap opening, and the formation of a charge-density wave (CDW). Their simulated STM images revealed an occurrence of charge ordering with a double periodicity along the borine wire. They also theoretically proposed a self-assembly technique for fabrication of the heterogeneous pyridine-borine wire on the dangling-bond (DB) wire generated on a H-passivated Si(001) surface [208]. Their first principles density-functional calculations suggested that pyridine is needed to dose the DB wire before borine dosing for the formation of the pyridine-borine wire.

Very recently, a combination of scanning tunneling microscopy and density functional theory calculations was used to examine the structures of 2,3-butanediol stereoisomers adsorbed on a Si(001) – 2×1 surface at room temperature [209]. In their study, it was found that most molecules

prefer to adsorb on the bridge between the ends of two adjacent dimers within the dimer row; this adsorption preference differs from that of alkene-type molecules, which undergo a cycloaddition reaction with a Si dimer on Si(001) surfaces as we will discuss later. Determination of the absolute chirality of (*R,R*)- and (*S,S*)-2,3-butanediol adsorbates on Si(001) indicated that each molecule preserves its chirality during bonding to Si atoms. In addition, 2,3-butanediol preferred to adsorb in the CH₃-gauche conformation rather than the CH₃-anti conformation, which can be explained by steric considerations. Similarly, they also studied the adsorption structures of benzene and pyridine on Si(5 5 12) – 2×1 at 80 K [210]. These structures were different from those observed on low-index Si surfaces: benzene molecules exclusively bind to two adatoms, that is, with di- σ bonds between carbon atoms and silicon adatoms, leading to the loss of benzene aromaticity; in contrast, pyridine molecules interact with adatom(s) through either Si–N dative bonding or di- σ bonds. It is very interesting that the dative bonding configurations with pyridine aromaticity are the dominant adsorption features and are more stable than di- σ bonding configurations, thus the dative bonding of nitrogen-containing heteroaromatic molecules provides a strategy for the controlled attachment of aromatic molecules to high-index surfaces.

The chemical reactions occurring on surface are generally very complicated, so computational studies are essential to better understand the molecular functions on surface. Sometimes, computational study encourages experimentalists to re-examine molecular functions and reactions on surface. A recent study by first principle calculations on the dissociation of water and ammonia on silicon surface showed that the dissociation of water and ammonia on Si(001) occurs via two facile reaction pathways [211–215]. In an earlier experiment, the adsorption of those molecules on Si(001) was interpreted under the assumption that the H dissociation occurs on the same dimer [216]. However, the computational study suggested that

such an interpretation [217,218] could be reexamined considering that inter-dimer dissociation could occur.

Cycloaddition reactions on silicon surface have been debated for times. Both computational and experimental studies have contributed a lot to understand the cycloaddition reactions on surface [219]. Early experimental [220–223] and theoretical [224] studies have shown that ethylene, propylene, and acetylene easily chemisorb on the Si(100) – 2×1 surface, yielding [2 + 2] products, and thermally stable up to 600 K. Theoretically, Liu and Hoffmann [225] studied the acetylene adsorption on the Si(100) surface, and found that a π -complex precursor and a biradical intermediate are involved in the cycloaddition reaction that has a low energy barrier to [2 + 2] cycloaddition products, consistently with the experimental findings. Recent experimental [226] and theoretical [227–230] studies found other possible surface products of acetylene, which brought about a new complexity to the surface reactions of ene systems. Since then, a lot of revisiting have been made to explore the cycloaddition reaction on silicon surface. Hamers and co-workers [231] studied the 2,3-dimethyl-1,3-butadiene reaction on the Si(100) – 2×1 surface, and the product was found to be from 80% of Diels-Alder product and 20% of [2 + 2] product. In the case of 1,3-cyclohexadiene, they further observed 55% of [4 + 2] products, 35% of [2 + 2] product, and 10% unknown. Therefore, there exists a competition between [4 + 2] and [2 + 2] reactions of the diene on the Si(100) surface. Subsequent theoretical studies [232–234] provided further support for the existence of competing reactions by showing that there exists a low energy [2 + 2] cycloaddition pathway on the Si(100) surface and that surface isomerization reactions connecting [4 + 2] and [2 + 2] products are very unlikely due to a high activation barrier. Minary and Tuckerman [235,236] recently considered the dynamic aspects of the cycloaddition reactions of 1,3-butadiene on the Si(100) – 2×1 surface with *ab initio* molecular dynamics. They showed that a stepwise zwitterionic mechanism governs the addition product formation. In addition, the initial and subsequent surface reaction mechanisms of 1,3-cyclohexadiene on the Si(100) – 2×1 surface were theoretically explored [237]. Multi-reference wave functions approaches was applied to study the ethylene and 2-butene surface reactions on Si(100) in their lowest energy singlet states [238].

CONCLUDING REMARKS

We have introduced several examples of computational approaches in supramolecular chemistry. However, due to the space limitation, we could not include much more computational applications that have been done. As introduced, current state-of-the-art

calculations can simulate NMR chemical shift, coupling constants, IR spectra, Raman spectra, UV-spectra, and STM images as well as stable structures and energetics. Though this short review covers only a small portion of the computational applications in supramolecular chemistry, similar approaches can be applied to many other supramolecular systems almost without limit. Most importantly, the collaborative works by computational and experimental studies are most encouraged in the supramolecular chemistry.

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