

# Theoretical investigations of intermolecular interactions involving $\pi$ -systems and their utility in the design of novel functional nanomaterials

P. Tarakeshwar\* and Kwang S. Kim\*\*

National Creative Research Center for Superfunctional Materials  
Department of Chemistry, Pohang University of Science and Technology  
San-31, Hyojadong, Namgu, Pohang 790-784, Korea.

\* tara@postech.ac.kr, \*\* kim@postech.ac.kr

## ABSTRACT

The design and development of novel functional nanomaterials has drawn intense interest because of their potential applications in electronics, physics, chemistry, biology, and medicine. An effective design strategy requires a thorough understanding of various interaction forces and mechanisms which prevail in such small dimensions. The wide manifestation of  $\pi$  systems in broad classes of nanomaterials ranging from organic polymers to fullerenes implies that a fundamental understanding of these intermolecular interactions from both theoretical and experimental perspectives would be of value. The present work initially details our efforts to theoretically investigate the characteristics of the interaction of these  $\pi$  systems (olefinic, aromatic, and fullerenes) with a wide range of countermolecules ranging from single atoms to rare gases to elemental hydrides to cations to Lewis acids. The information obtained from these theoretical investigations was then employed in the design of aesthetically appealing and functionally useful ionophores and organic nanotubes. The synthesis and characterization of the latter revealed the presence of infinitely long one-dimensional H-bond arrays. The relevance of these one-dimensional H-bond arrays in both material science and biology and the utility of this design strategy in developing functional nanosystems would also be discussed.

**Keywords:** Nanomaterial design, Functional nanosystems, Intermolecular interactions,  $\pi$  systems, Energy decomposition

## 1 INTRODUCTION

One of the fundamental issues in nanoscience and nanotechnology is the design of novel nanomaterials with specific and desirable properties [1]. While experimental measurements have made many important contributions over the years to enhance our understanding of these properties, 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]. However, theoretical description of these nanomaterials, which belong to the mesoscopic phase, is fraught with

a number of problems because neither quantum chemical methods, used to investigate the microscopic phase, nor solid state physics methods, used to investigate the macroscopic phase, can adequately describe all the desired properties [2, 3].

Against this background, it is of interest to improve the reliability of theoretical description of these nanomaterials by engaging the desirable features of both quantum chemical and solid state methods, so as to enable their use in the design of functional nanomaterials. In this context, intermolecular interactions involving  $\pi$  systems are of interest because they are observed in a wide variety of nanomaterials and are spread over a wide spectrum in terms of strength, origin, and their influence [4]. In particular, the strength and origin of the interaction depends both on the nature of the  $\pi$  system and the countermolecule interacting with it (Figure 1). The ability of theoretical methods in describing these interactions involving  $\pi$  systems also varies. Thus, stronger interactions involving metal cations are reliably described using relatively simple theoretical methods but interactions involving neutral molecules or rare gases require extremely sophisticated theoretical approaches [4].

Since, to the best of our knowledge, there have been few detailed studies of intermolecular interactions involving  $\pi$  systems using either quantum chemical or solid state physics method, it would be of interest to examine the nature of these interactions. Therefore the present study details some of the results obtained using the former approach [4–7]. The utility of this approach in the design of novel functional nanomaterials is then illustrated with a few examples [8–13].

## 2 METHODS

All the calculations reported in this study were carried out using the supermolecular (SM) variational and symmetry adapted perturbation theory (SAPT) methods [4, 14]. 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 [4]. On the other hand, SAPT enables one to obtain a physical picture of the interactions prevailing between the various complex monomers. This is because, in the SM method, the interaction energy is

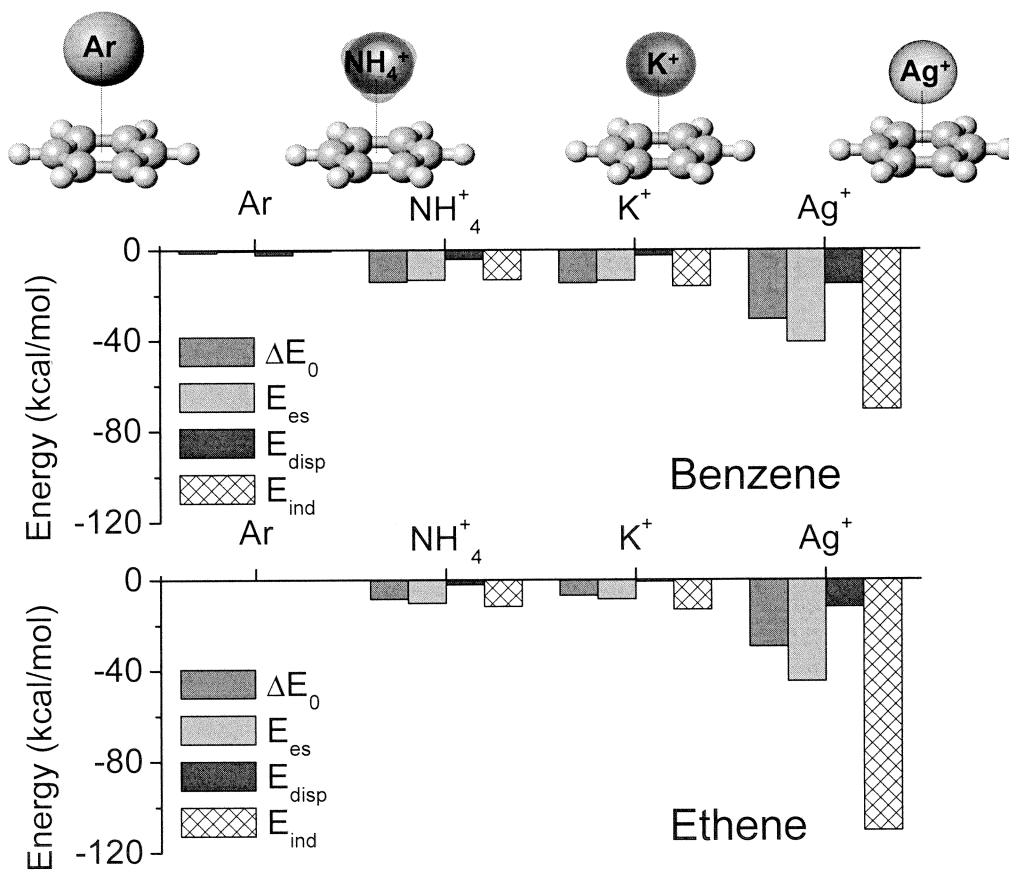


Figure 1: Magnitude of the total interaction energies ( $\Delta E_0$ ) and the individual interaction energy components of the argon, ammonium cation, potassium cation, and silver cation complexes of ethene and benzene. The optimized structures of the benzene complexes are displayed on the top.

evaluated as the difference of the energy of the complex and the energy of the isolated monomers. However, in the SAPT method, the interaction energy is obtained as a sum of the individual *electrostatic* ( $E_{es}$ ), *exchange* ( $E_{exch}$ ), *dispersion* ( $E_{disp}$ ), and *induction* ( $E_{ind}$ ) energies. All the SAPT calculations were carried out on the optimized geometries, which were obtained from the SM calculations [4]. Given the fact that all the intermolecular interactions involving these  $\pi$  systems are mediated through the  $\pi$  electron cloud, large basis sets which explicitly take into account its diffuse nature, were employed in the calculations [4–7]. All the SM calculations were carried out at the second order Møller-Plesset (MP2) level of theory [15], because of the importance of electron correlation in describing these complexes and the inability of density functional methods to account for this electron correlation [4].

### 3 RESULTS AND DISCUSSION

The wide variation of the strength and origin of the intermolecular interactions involving  $\pi$  systems can be noted from Figure 1. Thus the replacement of the argon atom in the benzene-Ar complex with a silver cation results in an increase of the interaction energy ( $\Delta E_0$ ) from 0.97 to  $\sim 39.2$  kcal/mol. The general notion of strong interactions involving cations having only an electrostatic origin is dispelled by the magnitude of the induction energies given in Figure 1. Dispersion energies, whose magnitudes are small when compared to either the electrostatic or induction energies in case of the  $\pi$ -cation complexes, are however crucial in case of the rare gas complexes. This is because of the fact that the sum of both the electrostatic and induction energies is too small to overcome the large exchange repulsion energy [7].

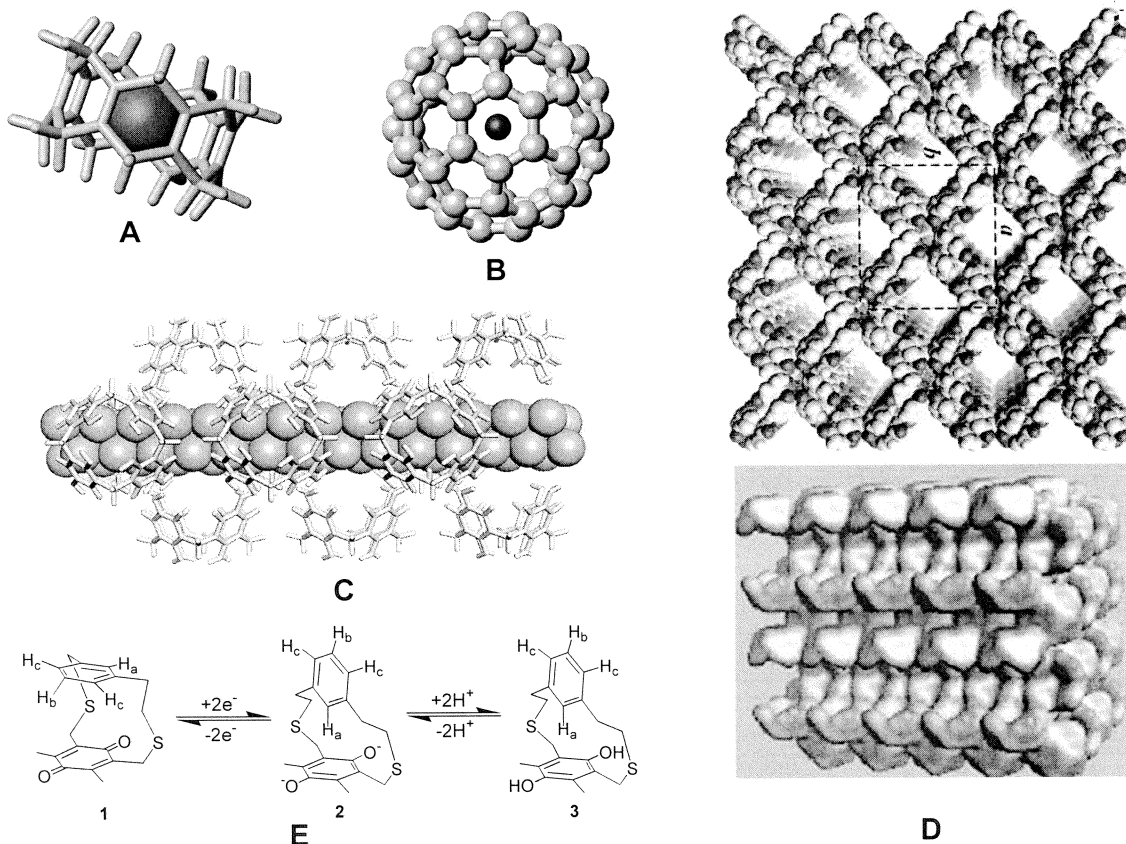


Figure 2: Examples of designed nanomaterials: (A) [7]beltene-K<sup>+</sup>, (B) endohedral fullerene with paramagnetic atom, (C) formation of a nascent silver wire in the calix[4]hydroquinone organic nanotube, (D) experimental profiles of the calix[4]hydroquinone honeycomb, (E) schematics of a nanoelectromechanical device.

Similar observations have been made for the interaction of these  $\pi$  systems with neutral molecules like methane and hydrogen fluoride [4–6]. Thus, the interactions involving hydrogen fluoride are dominated by induction and electrostatic energies and those involving methane by dispersion energies.

It can be noted from Figure 1, that the magnitude of the interaction energies ( $\Delta E_0$ ) in the  $\text{Ag}^+$ - $\pi$  complex, is nearly independent of the nature of the  $\pi$  system. This is interesting, because the intrinsic flexibility of ethene as compared to the more rigid benzene can be harnessed to design useful nanomaterials. This is the essence of a recent study [8], wherein we have investigated the cation complexing abilities of ionophores (beltenes) (Figure 2A) containing olefinic double bonds. We have found that these beltene exhibit strong affinities and high selectivity for alkali metal cations. Com-

pared to a related aromatic system containing ionophore (collarenes) [9], the beltene, with more flexible cavities, were found to exhibit finer ion selectivity. Additionally, we also observed that suitable substituents could be employed to enhance both the binding and specificity of various sizes of these beltene to different cations, as well as to increase their solubility [8].

Our calculations on the ethene and benzene complexes of rare gases and the reports of the experimental observation of endohedral C<sub>60</sub> complexes of paramagnetic atoms [7, 16], led us to an interesting correlation of interactions involving benzene and C<sub>60</sub>. Our calculations on benzene...A and endohedral AC<sub>60</sub> (Figure 2B), where A is a paramagnetic atom like nitrogen, phosphorous, oxygen or sulfur, revealed (Figure 3) that the interaction energies of the C<sub>60</sub> complexes are nearly ten times those of benzene...A and five times that of

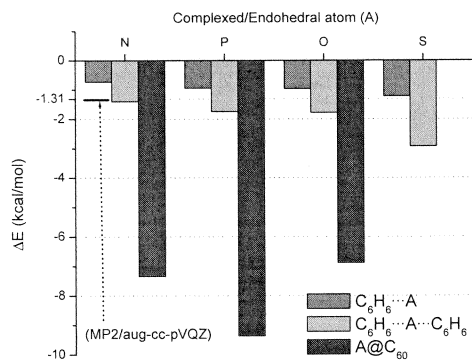


Figure 3: Magnitude of the interaction energies ( $\Delta E_e$ ) of the complexes of benzene and  $C_{60}$  with the paramagnetic nitrogen, phosphorous, oxygen, and sulfur atoms. The energies have been obtained at the MP2/6-31G\* level. The value obtained at the MP2/aug-cc-pVQZ level for the benzene...N complex is also shown for comparison.

benzene...A...benzene sandwiched complex [10]. We also noted that the interaction energies of these  $\pi$  complexes of paramagnetic atoms are dominated by dispersion energies. This correlation of the interaction energies of benzene and  $C_{60}$  complexes is very useful because the latter, unlike the former, are not amenable to high level theoretical calculations.

In order to highlight the applicability of the aforementioned results in the design of functional nanomaterials, we discuss two recent examples of the experimental realization of ultrathin nanowires [11, 12] and nanomechanical devices [13]. The electrostatic origin of the interaction energies involving  $\pi$  systems and cations implied that a modulation of the  $\pi$  electron density would significantly influence both the nature and magnitude of the binding. This together with the reduction properties of the quinone molecule was harnessed to fabricate ultrathin silver nanowires (Figure 2C) within the pores of the calix[4]hydroquinone molecule (Figure 2D) [11, 12]. A clever synthesis of an organic molecule containing both benzene and quinone moieties yielded a novel nanomechanical device, which can be electrochemically controlled (Figure 2E) [13].

#### 4 CONCLUSIONS AND OUTLOOK

In the present study, we have highlighted the importance of theoretical investigations of intermolecular interactions involving  $\pi$  systems in an understanding of their magnitude and origin. As can be seen from the results, the magnitudes and origin of the interaction energies are dependent both on the nature of the  $\pi$  system and the counter molecule interacting with it. Though

not discussed here, our calculations indicate that the magnitude of the repulsive energies has a crucial role in governing the equilibrium geometries of these complexes [4–7].

This understanding was put to use in the design and development of novel functional nanomaterials. We believe that this strategy of a theoretical design preceding the actual experimental work is a useful approach because it helps obtain hitherto unknown information on the nature of the sought nanomaterial.

Though most of the calculations reported in this study were carried out using the quantum chemical approach, efforts are currently underway to extend the capabilities of the solid state physics approach in describing the properties of these intermolecular complexes containing  $\pi$  systems.

#### 5 ACKNOWLEDGEMENTS

Financial support for this work was provided by the Creative Research Initiative Program of the Korean Ministry of Science and Technology.

#### REFERENCES

- [1] A. P. Alivisatos, P. F. Barbara, A. W. Castleman, et al., *Adv. Mater.* 10, 1297, 1998.
- [2] H. Haberland (Ed.) "Clusters of Atoms and Molecules," Springer-Verlag, 1994.
- [3] M. L. Cohen, *Mat. Sci. Eng. C*, 15, 1, 2001.
- [4] K. S. Kim, P. Tarakeshwar, and J. Y. Lee, *Chem. Rev.* 100, 4145, 2000.
- [5] P. Tarakeshwar, H. S. Choi, S. J. Lee, et al., *J. Chem. Phys.* 111, 5838, 1999.
- [6] P. Tarakeshwar, H. S. Choi, and K. S. Kim, *J. Am. Chem. Soc.* 123, 3323, 2001.
- [7] P. Tarakeshwar, K. S. Kim, E. Kraka, et al., *J. Chem. Phys.* 115, 6018, 2001.
- [8] H. S. Choi, D. Kim, P. Tarakeshwar, et al., *J. Org. Chem.* 67, 1848, 2002.
- [9] H. S. Choi, S. B. Suh, S. J. Cho, et al., *Proc. Natl. Acad. Sci. USA* 95, 12094, 1998.
- [10] J. M. Park, P. Tarakeshwar, K. S. Kim, et al., *J. Chem. Phys.* 116, 10684, 2002.
- [11] B. H. Hong, C.-W. Lee, J. Y. Lee, et al., *J. Am. Chem. Soc.* 123, 10748, 2001.
- [12] B. H. Hong, S. C. Bae, C.-W. Lee, et al., *Science* 294, 348, 2001.
- [13] H. G. Kim, C.-W. Lee, S. Yun, et al. *Org. Lett.* 4, 3971, 2002.
- [14] B. Jeziorski, R. Moszynski, and K. Szalewicz, *Chem. Rev.* 94, 1721, 1994.
- [15] C. Møller and M. S. Plesset, *Phys. Rev.* 46, 618, 1934.
- [16] T. Almeida Murphy, T. Pawlik, A. Weidinger, et al., *Phys. Rev. Lett.* 77, 1075, 1996.