Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

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Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional organic materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies. In this project, novel functional organic materials based on various heterocycles were synthesized and their physical and structural properties were investigated.

1. A Linear Chain of Water Molecules Accommodated in a Macrocyclic Nanotube Channel[1)]

A macrocyclic tetramer of 2-phenyl-1,3,4-oxadiazole was synthesized, and its self-assembly was investigated. The macrocycle was stacked to form a one-dimensional (1D) columnar structure containing water molecules. The nanotube self-assembled into a bundle, which grew into a molecular wire. The association of the water molecules in the tubular cavity resulted in shielding of the 1D chain of water molecules by the nanotube; these macrocyclic nanotube channels are promising candidates for nanotechnological applications.

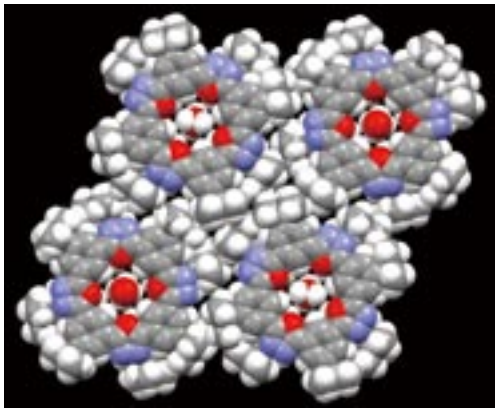

Figure 1. Bundle structure of the microcyclic nanotube.

2. Theoretical Study of Noncovalent Interactions Between Triple Bonds and Chlorine Atoms in Complexes of Acetylene and Some Chloromethanes[2)]

The intermolecular potential surfaces of the acetylene–chloromethane complexes containing C–Cl···π (triple bond) interaction were calculated by the HF and MP2 methods with cc-pVXZ (X = D, T, Q) basis sets. At the minimum, the intermolecular distances between the triple bond and chlorine atom range from 3.3 to 3.5 Å. The CCSD(T) method predicted that the binding energies of the acetylene complexes with CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are –0.49, –0.77, –1.05 and –1.34 kcal/mol at the basis set limit, respectively.

3. Theoretical Study for a Complex of 1,2,5-Thiadiazole with Formic Acid[3)]

Ab initio and DFT calculations have been performed on a complex of 1,2,5-thiadiazole with formic acid. Fifteen local minima of the complex are found using the MP2/6-31G method. The three stable structures with the lowest total energies are examined at the HF, MP2 and B3LYP/6-311++G(2d,2p) levels. The first and second stable structures contain intermolecular O–H···N/C–H···O and S···O/O–H···N interactions, respectively. Their binding energies by MP2 corrected BSSE and ZPE are –7.0 and –7.2 kcal/mol, which indicate a great stabilization of the complex.

References

1) K. Ono, K. Tsukamoto, R. Hosokawa, M. Kato, M. Suganuma, M. Tomura, K. Sako, K. Taga and K. Saito, *Nano Lett.* **9**, 122–125 (2009).
2) M. Tomura, *Chem. Phys.* **359**, 126–131 (2009).
3) M. Tomura, *THEOCHEM* **868**, 1–5 (2008).