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Computational quantum chemistry study of a self-assembled Zn(II) porphyrin box

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Abstract

Motivation. The present study is motivated by a recent spectroscopic study of a self-assembled Zn(II) porphyrin box. Although experimental evidence based on NMR spectroscopy, gel-permeable chromatography and cold spray ionization – mass spectrometry indicates that the title porphyrin box do exists in solution, details of its atomic structure are not yet available. This study aims to provide a realistic 3D model of the porphyrin box which will be useful in assisting the interpretation of spectroscopic results.

Method. Two theoretical methods have been employed in this study, namely density functional theory (DFT) and semiempirical MO theory. As for the former theory, we employed the BLYP method which combines the exchange functional of Becke with the correlation functional of Lee-Yang-Parr. As for the latter theory, we employed the MNDO method of Dewar and Thiel which is based on the NDDO approximation.

Results. The atomic structure of the Zn(II) porphyrin box has been successfully optimized and the corresponding frontier MO have been analyzed. It is shown that the box is actually a parallelepiped rather than a cube as previously suggested. Furthermore, both HOMO and LUMO are localized on one monomer unit only, which comprises a pair of covalently linked Zn(II) porphyrins. The energy gain associated to the self-assembly of four monomers corresponds to about 61 kcal/mol.

Conclusions. The atomic model of the Zn(II) porphyrin will be useful in assisting the interpretation of the spectroscopic results and represents the starting point for theoretical studies of the excited states.

Keywords. Self-assembly; supramolecular chemistry; Zn(II) porphyrin box; computational quantum chemistry; BLYP; MNDO.

Abbreviations and notations

NDDO, neglect of diatomic differential overlap	MNDO, modified neglect of differential overlap
BLYP, Becke-Lee-Yang-Parr method	DFT, density functional theory
HOMO, highest-occupied molecular orbital	LUMO, lowest-unoccupied molecular orbital
MO, molecular orbital	NMR, nuclear magnetic resonance
GPC, gel-permeable chromatography	CSI-MS, cold spray ionization – mass spectrometry

1 INTRODUCTION

There exists considerable interest in the synthesis of 2D and 3D porphyrin arrays (1D being a single porphyrin molecule) for possible applications in molecular electronics, artificial photosynthesis, and molecular-scale optical devices [1]. For example, 2D orthogonal and fused porphyrin arrays (fused 2D porphyrin arrays are also called porphyrin tapes) containing a variety of metal ions might be employed as molecular wires in the future generation of molecular-scale electronic devices and nanocomputers. 3D porphyrin arrays have been synthesized starting from the parent 2D specie. These porphyrin arrays display a certain degree of conformational freedom owing to the possibility of rotation through single C-C bonds connecting neighboring porphyrins.

A compact 3D porphyrin array whose structure resembles that of a cube (or box) has been

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obtained from the self-assembly of orthogonally linked porphyrin dimers [2]. Owing to its structural rigidity and the spatial location of the eight Zn(II) ions, the title porphyrin box displays unique photophysical properties, in particular a blue shift in the low-energy Soret band.

In spite of its uniqueness, however, the molecular structure of this porphyrin box has not been yet characterized by single-crystal X-ray diffraction crystallography. One of the possible reasons for this might be due to difficulties in the growth of good-quality single-crystals form solution. In this regard, Kim, Osuka and their coworkers have observed that the self-assembly of the porphyrin box in solution critically depends upon the type of solvent employed [2]. As a result, the box forms in CH_2Cl_2 since this solvent does not coordinate the Zn(II) ion whereas in other solvents the box cannot self-assemble. Nevertheless, by employing ^{1}H-NMR spectroscopy, gel-permeable chromatography (GPC), and cold spray ionization-mass spectrometry (CSI-MS) they inferred the 3D structure of the Zn(II) porphyrin box whose metal framework is schematically shown in Figure 1. The Zn•••Zn distance in their idealized model corresponds to 8 Å.

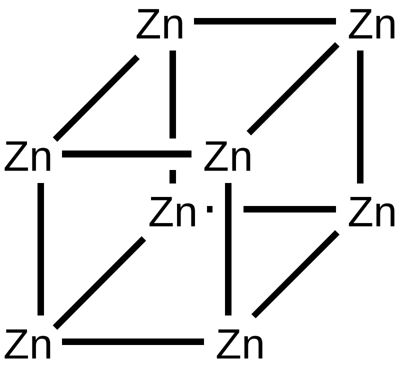

Figure 1. Metal framework of the Zn(II) porphyrin box.

It is obvious, however, that the availability of an atomic model of the porphyrin box should be quite useful in further rationalizing the experimental results so far obtained as well as in shading light on its electronic structure. Computational quantum chemistry methods come to the rescue. Accurate molecular structures can be obtained from computational quantum chemistry methods such as density functional theory (DFT), ab initio Hartree-Fock (HF), and semiempirical molecular orbital (MO) theory [3]. The latter methods are particularly important in studying the molecular and electronic structures of large systems such as giant molecules [4] and proteins [5]. Here we employ semiempirical MO methods to characterize, for the first time, the molecular and electronic structure of the Zn(II) porphyrin box and its parent monomer. Furthermore, DFT calculations are also performed on its parent Zn(II) porphyrin monomer so as to assess the results obtained with the semiempirical method.

2 COMPUTATIONAL METHODS

All the quantum chemical calculations have been performed with the parallel version of the Gaussian 03 (Revision B.05) software package [6]. The semiempirical MNDO method [7] based on the neglect of diatomic differential overlap (NDDO) approximation [8] was employed to optimize the structures of the porphyrin box and that of its parent monomer. Density functional theory (DFT) calculations with the BLYP exchange-correlation functional [9,10] and the 3-21G basis set [11] were also performed on the monomer. BLYP is a pure DFT method that combines Becke's 1988 exchange functional [9] with the correlation functional of Lee-Yang-Parr [10].

The WinMopac3.9 package [12] was employed to visualize the molecular orbitals and electron densities of the molecules investigated herein.

3 RESULTS AND DISCUSSION

We started our investigation with the geometry optimization of the parent monomer of **1**, which is made of two Zn(II) porphyrin units linked through a single C-C bond and bearing two pyridyl groups at two meso positions, as shown in Figure 2.

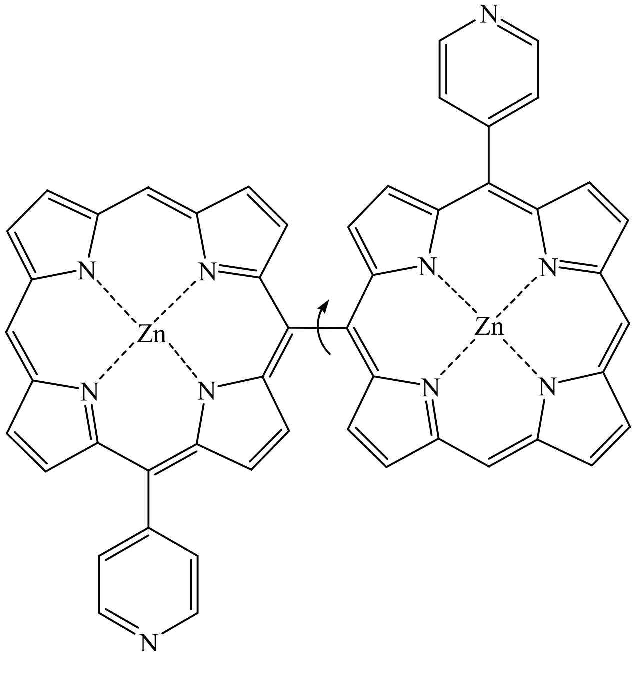

Figure 2. Schematic structure of the binuclear Zn(II) porphyrin monomer.

The presence of a single C−C bond connecting the two porphyrin units would suggest the possibility of free rotation through this bond. However, steric contacts between the C−H bonds of neighboring pyrrolo units favor two rotamers (Figure 3) having the porphyrins' molecular planes oriented perpendicularly to each other. The two rotamers are enantiomers since their structures cannot be superimposed on each other through any rotation□translation operation.

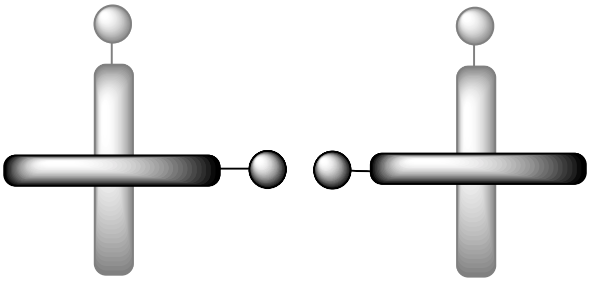

Figure 3. Projection of the rotamers as viewed along the Zn-Zn internuclear axis.

Figure 4 shows the molecular structure of the dinuclear Zn(II) porphyrin monomer as optimized with both the BLYP/3-21G and MNDO methods. The main difference between these optimized structures is seen in the orientation of thir pyridyl moieties. The pyridyl moieties of the DFT-optimized dimer (Figure 4a) are tilted by 68 and -68 degrees, respectively, whereas those in the MNDO-optimized dimer (Figure 4b) are perpendicularly oriented with respect to the corresponding porphyrin molecular plane. The interatomic distances between Zn(II) centres are in excellent agreement being at 8.501 Å (BLYP/3-21G) and 8.499 Å (MNDO), respectively. The length of the C-C bond connecting the porphyrin units is at 1.514 Å (BLYP/3-21G) and 1.504 Å (MNDO), respectively. The magnitude of the dipole moment associated to the dimer corresponds to 3.4 Debye, as computed at the BLYP/3-21G level of theory.

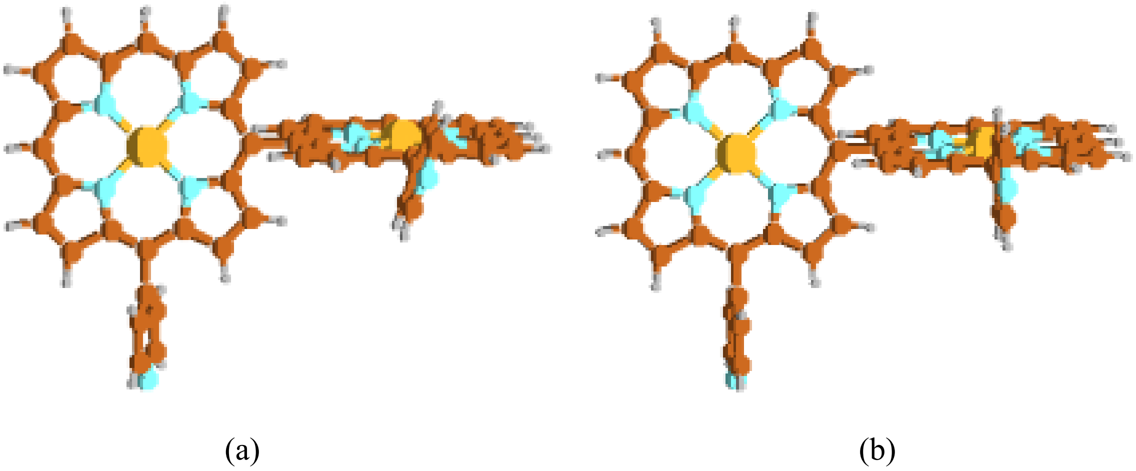

Figure 4. Molecular structure of the dinuclear Zn(II) porphyrin monomer as optimized with the (a) BLYP/3-21G and (b) MNDO methods.

The porphyrin box results from the self-assembly of four dimer units. Given its large size (360 atoms), its geometry was optimized with the MNDO method only. Figure 5 shows the optimized structure of the porphyrin box. The energy gain resulting from the self-assembly process corresponds to about 61 kcal/mol. This amount of energy corresponds roughly to the formation of eight Zn−N coordination bonds. The cubic box formed by the Zn(II) ions has linear dimensions of 8.55 Å *x* 10.16 Å *x* 10.16 Å. The Zn(II)•••Zn(II) distance along one diagonal corresponds to 14.37 Å while that along the tridiagonal is at 16.701 Å.

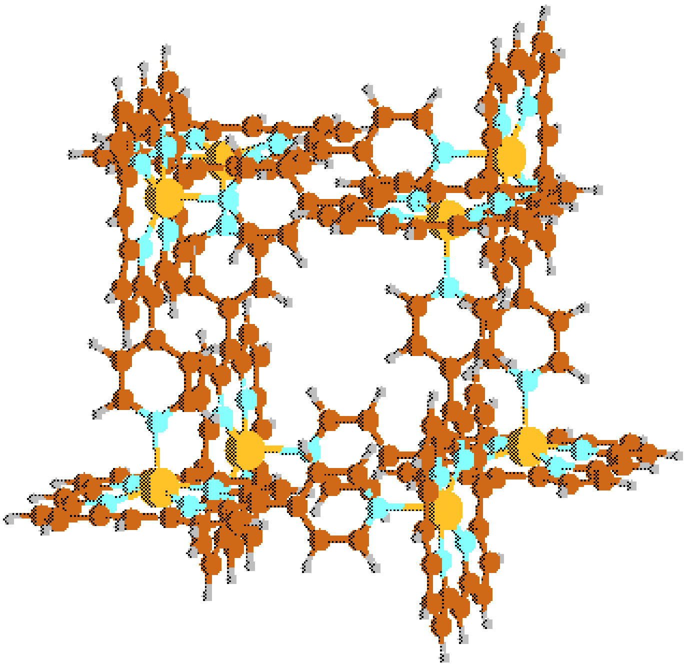

Figure 5. Optimized molecular structure of the Zn(II) porphyrin box (tetramer).

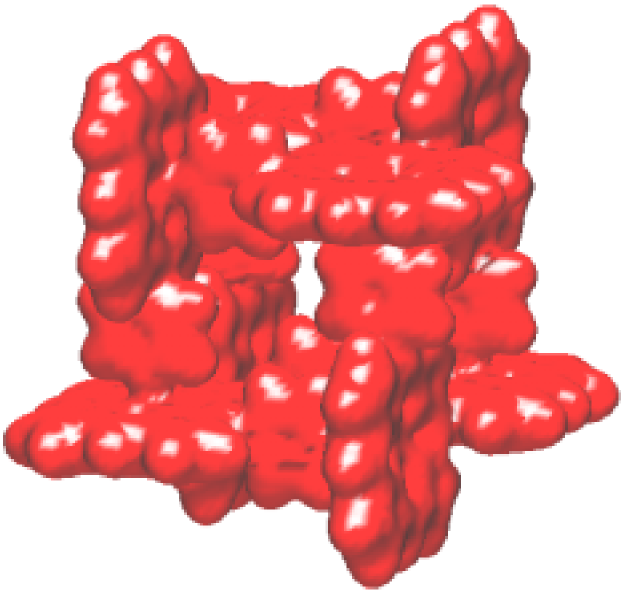

Figure 6. Total electron density of the Zn(II) porphyrin box.

Figure 6 shows the total electron density of the Zn(II) porphyrin box as calculated with the MNDO method. As it appears from this figure, the center of the box is empty thereby indicating that this cavity could be utilized to host a small molecule. In Figure 7 are shown the frontier orbitals of the porphyrin box. Interestingly, both HOMO and LUMO are localized on one monomer unit only. This is not so, however, for HOMO-2 and HOMO-3 both of which are localized on two monomer units. We expect this result being useful in the interpretation of the spectroscopic experiments.

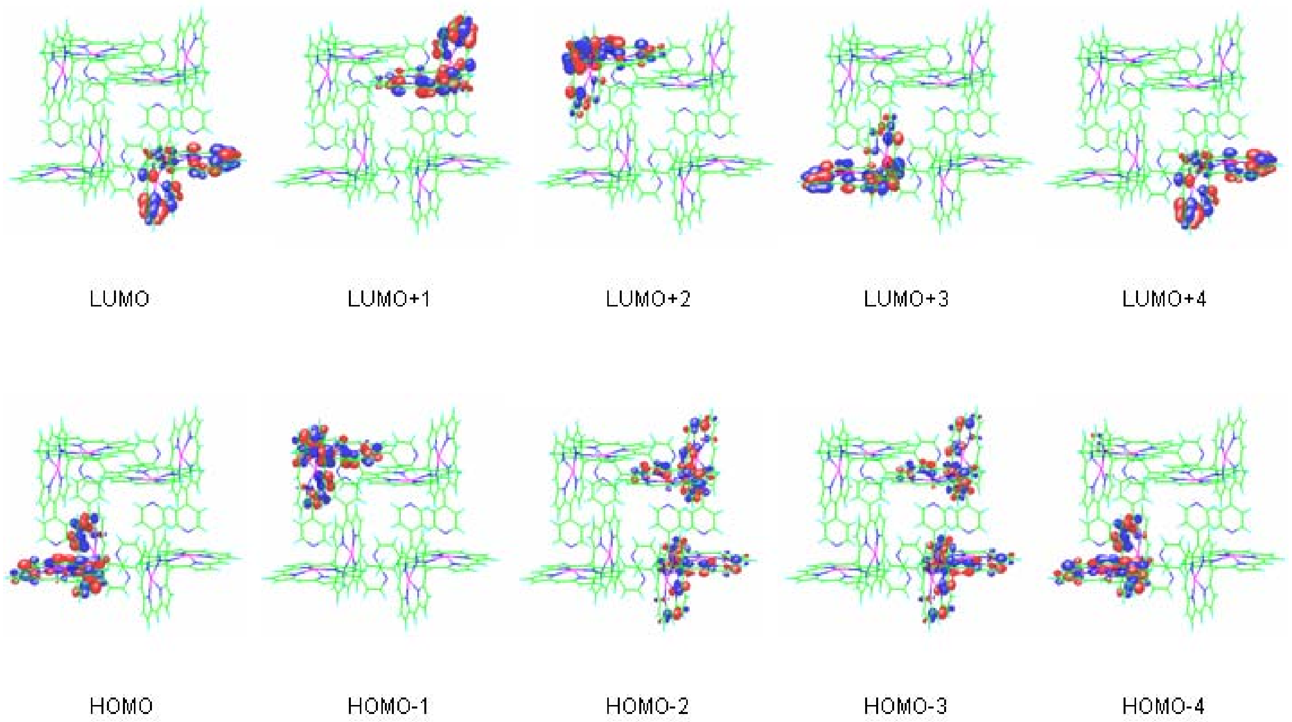

Figure 7. Frontier orbitals of the Zn(II) porphyrin box.

4 CONCLUSIONS

We presented the first computational quantum chemistry study of the Zn(II) porphyrin box and its parent monomer unit. The optimized molecular geometry of the box shows that this supramolecular structure is not a perfect cube but a parallelepiped since one of its dimensions is slightly shorter than the other two. The analysis of the frontier orbitals is expected to be useful in assisting the interpretation of the spectroscopic experiments.

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Supplementary Material

The Cartesian coordinates of the molecules herein investigated are available from the author upon request.

5 REFERENCES

[1] D. Kim and A. Osuka, Directly Linked Porphyrin Arrays with Tunable Excitonic Interactions, *Acct. Chem. Res.* **2004**, *37,* 735-745.

[2] A. Tsuda, T. Nakamura, S. Sakamoto, K. Yamaguchi and A. Osuka, A Self-Assembled Porphyrin Box from *meso,meso* Linked Bis-{5-p-pyridil-15-(3,5-di-octyloxyphenyl)porphyrinato Zinc(II)}, *Angew. Chem., Int. Ed.* **2002**, *41*, 2817-2821.

[3] C.J. Cramer, *Essentials of Computational Chemistry,* John Wiley & Sons, Chichester, 2002.

[4] F. Pichierri, Cubanoids: Computer-Aided Molecular Design of Compact Hydrocarbons Constructed by Assembling Cubane Units, *Internet Electron. J. Mol. Des.* **2004**, *3*, 134-142.

[5] F. Pichierri, Computation of the Permanent Dipole Moment of a-Chymotrypsin from Linear-Scaling Semiempirical Quantum Mechanical Methods, *J. Mol. Struct. (Theochem)* **2003**, *664-665*, 197-205.

[6] M.J. Frish *et al.*, Gaussian 03 (revision B.05), Gaussian, Inc., Pittsburgh PA, 2003.

[7] M.J.S. Dewar and W. Thiel. Ground States of Molecules, 38. The MNDO Method. Approximations and Parameters, *J. Am. Chem. Soc.*, **1977**, *99,* 4899-4907.

[8] W. Thiel, Perspectives on Semiempirical Molecular Orbital Theory, *Adv. Chem. Phys.* **1996**, *93*, 703.

[9] A.D. Becke, *Phys. Rev. A* **1988**, 38, 3098.

[10] C. Lee, W. Yang, and R.G. Parr, *Phys. Rev. B* **1988**, *37,* 785.

[11] J.S. Binkley, J.A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.* **1980**, *102,* 939.

[12] WinMOPAC (version 3.9), Fujitsu Limited, Tokyo.

Biography

Fabio Pichierri is associate professor at Tohoku University (Sendai). He studied theoretical and structural chemistry at the University of Trieste (1985-1995) and was awarded the Ph.D. in Chemical Sciences from the University of Roma in 1996. Soon after the completion of his PhD, he moved to Japan where he did postdoctoral research at RIKEN (The Institute of Physical and Chemical Research) and the research centre of Mitsubishi Chemical Corporation. In January 2003 Dr. Pichierri joined Tohoku University to carry out both teaching and research activities under the 21st century Center of Excellence (COE) project “Giant Molecules and Complex Systems” of MEXT. The main scientific accomplishments of Dr. Pichierri comprise the first realistic quantum mechanical (QM) computation of a protein macrodipole (α-chymotrypsin) by means of linear-scaling semiempirical QM methods, the design of a novel class of compact hydrocarbon molecules termed *cubanoids*, and the original proposal (based on quantum chemical calculations) of using fullerene anions as propellants for ion engines. Dr. Pichierri is an advisory board member of the International Association of Nanotechnology (IANT), a life member of the World Association of Theoretically Oriented Chemists (WATOC), and a member of the Chemical Society of Japan (CSJ), the Japanese Society of Applied Physics (JSAP), the Materials Research Society (MRS), and the Electric Space Propulsion Society (ESPC). F.P. is married and the father of two children.