Conformational Dependent Energy Migration on Cyclic Porphyrin Arrays

Suwhan Song, Minwoo Han, and Eunji Sim

Department of Chemistry and Institute of Nano-Bio Molecular Assemblies,
Yonsei University, 50 Yonsei-ro Seodaemun-gu, Seoul 120-749 Korea
E-mail: esim@yonsei.ac.kr

Intramolecular energy migration in a cyclic porphyrin array is spontaneous transfer of energy from one excited site to another. Since the efficiency of energy migration is inversely proportional to distance, the energy migration is occurred on their adjacent sites more often than distant ones. Therefore, the energy migration in the cyclic porphyrin array is largely dependent on their conformational characters. However, evaluation of conformational information by means of experimental tools is ambiguous since their limited resolution. In this work, we calculate the internal angle and distance distributions of cyclic porphyrin arrays using molecular dynamics simulations to obtain conformational information. To evaluate the angle and distance distributions respect to molecular size, we constructed molecules with n porphyrin dimers (n=1,3,7) in implicit solvent environment. Performing molecular dynamics simulations, we modulated alkyl groups to investigate additional conformational effects of the system.

Key Words : Energy Migration, Cyclic Porphyrn Array, Molecular Dynamics Sibulation

Introduction

As understanding the nature′s energy transfer, photosynthesis is an important process. Plants convert light energy into chemical energy during photosynthesis and this energy is provided to living organisms. Recently many researches have been investigated to duplicate the nature of photosynthesis to simplified systems for the sake of mimicking the abilities of natural light-harvesting and efficient excitation energy migration.[1] One of the most interesting systems is large macrocyclic molecules, which is similar to the natural light-harvesting complexes[2] and is potentially applicable to organic electronics. For this purpose, cyclic porphyrin arrays have drawn attention due to their efficient excitation energy transfer in a cyclic manner.

Figure 1 shows the feature of a cyclic porphyrin array, an artificial light-harvesting complex. The excitation energy transfer of porphyrin chromophores is the critical factor that determines various photophysical functions of the porphyrin array. Note that excitation energy hopping process of light-harvesting complexes depends on the interconnection length between chromophores[3]; the efficiency of energy migration is inversely proportional to the length between pigments. In other words, one can utilize conformational information to predict and elucidate energy migration of artificial light-harvesting complexes.
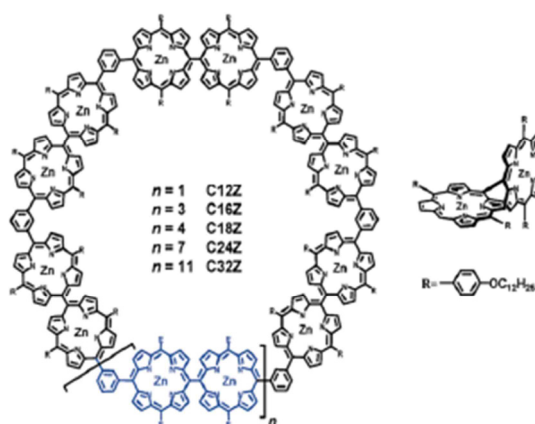
[Figure 12] Cyclic porphyrin arrays

However, measurement of conformational dimension by means of experimental tools is ambiguous. In this study, we focus on a simple simulation method for efficient computations of conformational information of cyclic porphyrin arrays. Using molecular dynamics (MD) simulation employing readily available force fields, we calculated dimer-dimer distances and angle distributions of cyclic porphyrin arrays by varying side-chain alkyl groups. On the basis of this strategy, we modeled various cyclic porphyrin arrays CnZ such as C12Z, C16Z and C24Z.[4]

Theory and Computational Method

Excitation energy hopping is the energy transfer between two light sensitive molecules like chromophores. Energy transfers from an electronically exited donor chromophore to an acceptor chromophore. The efficiency of this process is inversely proportional to the distance between two molecules through Förster equation[5] given as follows

$$k_{ET}(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 \qquad (1)$$

where τ_D is the excited-state lifetime of donor; R_0 is the Förster radius; r is the interchromophoric distance between donor and acceptor. Eq. (1) states that energy migration occurs more efficiently as inter-chromophore distance decreases. To further support size-dependent conformational change associated with spectral changes, we performed MD simulations on cyclic porphyrin arrays using the NAMD program with 2b8 version of CHARMM general force field. 0.9.7.1 version of CGenFF program was used for efficient parameterization. After several steps of minimization, 10 ns of product run was performed with 1 fs integration time step. Langevin thermostat was used to maintain the temperature at T = 298.15 Kelvin during the simulation. Dielectric constant, ε_r = 2.4, used for implicit solvent condition of toluene medium. For further analysis, we recorded atomic coordinates every 0.5 ps and obtained 16,000 different molecular conformations.

Results and Discussion

In order to identify the conformational information of cyclic porphyrin arrays, we calculated adjacent chromophore's exterior angle distribution and dimer-dimer distances of C12Z, C18Z and C24Z in room temperature. Angle distribution of cyclic porphyrin arrays are shown in Figure 2(a). Assuming perfectly planar conformation for CnZ arrays, the exterior angle should decrease as the ring size increases from C12Z to C24Z. In Figure 2(a), however, the angle distribution fluctuates. This indicates that cyclic porphyrin arrays have various structures rather than the planar conformation. Distances between chromophores of C12Z, C18Z and C24Z are shown in Figure 2(b). Distance distribution also suggests non-planar conformation characters because the distance decreases as the number of chromophores increases. To investigate side-chain effect on the conformations of cyclic porphyrin arrays, we also modeled C12Z, C18Z and C24Z molecules with several lengths of alkyl groups and their angle distributions are shown in Figure 3. As increasing the number of carbons in the alkyl group from 0 to 12, the exterior angle shifts to bigger values. Thus, inter-chromophore length of cyclic porphyrin arrays decreases with respect to the length of substituting alkyl groups. To investigate the influence of the substituting alkyl groups on the conformation of cyclic porphyrin arrays, we calculated the dimer-dimer distances. In Figure 4, distances between chromophores decreases as the length of alkyl substituent group increases.
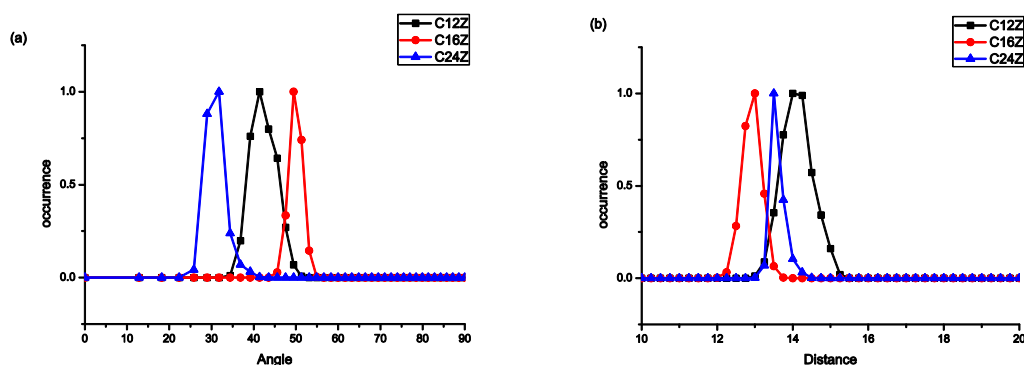

Figure 2. (a) Angle distribution of C12Z, C16Z and C24Z
(b) Distance distribution of C12Z, C16Z, and C24

The angle and distance results demonstrate that the cyclic porphyrin arrays have non-planar structures and cyclic porphyrin arrays with alkyl groups have closer chromophores than those with no alkyl substituents. In other words, cyclic porphyrin arrays with alkyl substituents migrates the excitation energy efficiently between chromophores.
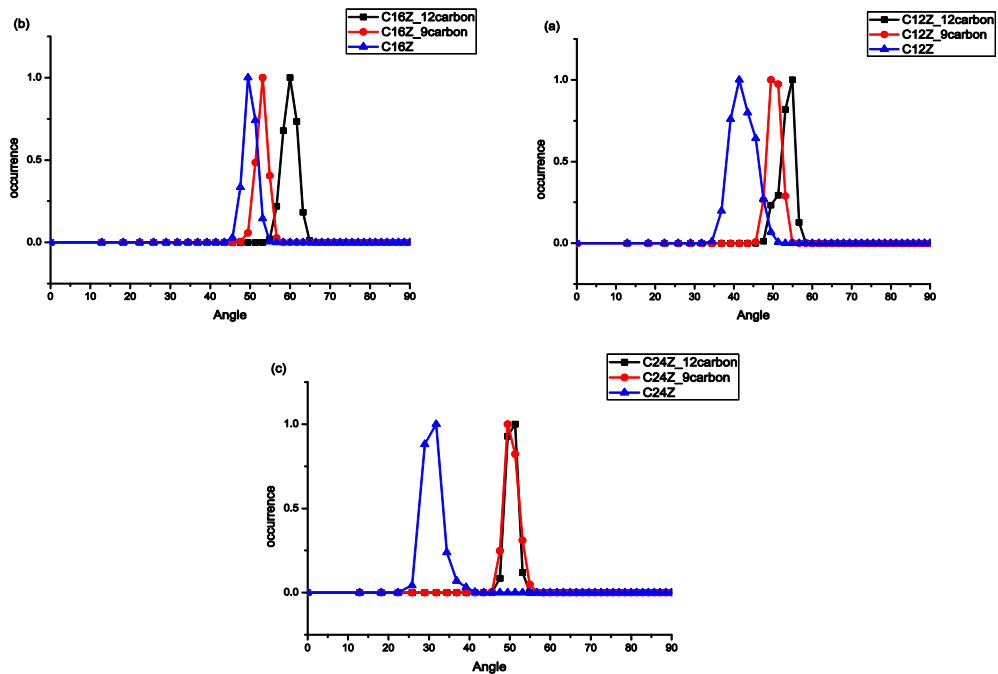
Figure 3. Angle distribution of (a) C12Z (b) C16Z (c) C24Z with no alkyl group(blue), alkyl group with 9 carbons(red), and 12 carbons(black)
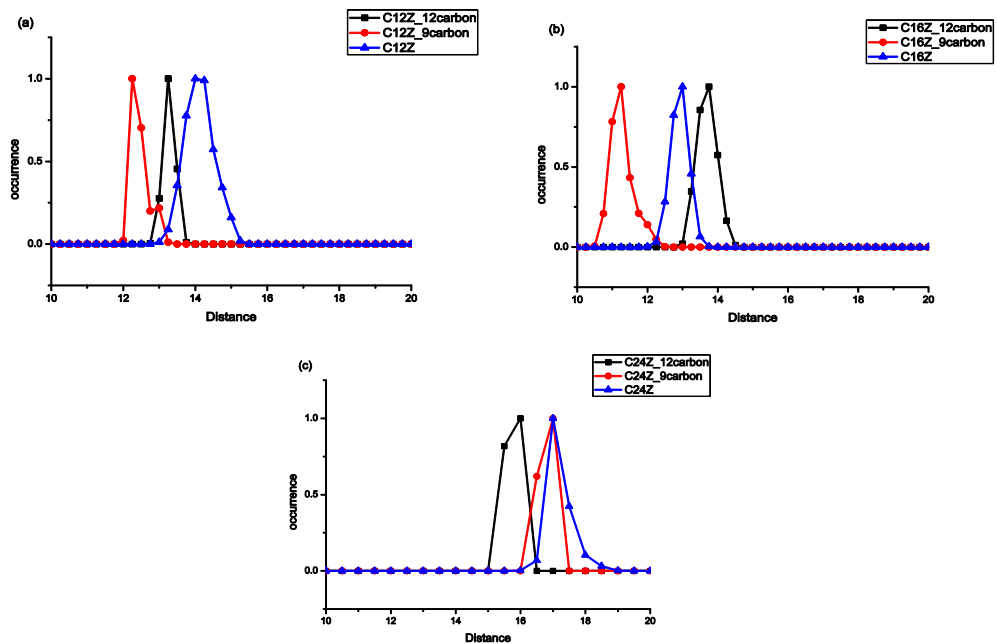
Figure 4. Distance distribution of (a) C12Z (b) C16Z (c) C24Z with no alkyl group(blue), alkyl group with 9 carbons(red), and 12 carbons(black)

Conclusion

We introduce a simple and intuitive computational method that is efficient and inexpensive for investigating conformations of artificial light-harvesting complexes. Conformational information of various cyclic porphyrin arrays were discussed in terms of dimer-dimer exterior angles and inter-dimer distances. Cyclic porphyrin arrays showed non-planar conformational characters with distributions of angles and distances. Since energy migration is affected by inter-dimer distance, conformational characteristics is important for artificial light harvesting molecules. The results suggest that, to increase the energy migration efficiency, substituting alkyl groups on the cyclic porphyrin array is useful. Alkyl substituents, in fact, help chromophores stay closer to each other, giving rise to the conformation with shorter intrachromophore distance, so that the excitation energy transfer rate increases according to the Förster equation.

Acknowledgements

Reference

1. Aratani, N.; Acc. Chem. Res. 2009, 42, 1922–1934.
2. Pullerits, T.; Acc. Chem. Res. 1996, 29, 381–389.
3. Roszak, A. W.; *Science* **2003**, *302*, 1969
4. Hori, T.; Chem.sEur. J. 2008, 14, 582
5. Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.