

Investigation of Chlorophylls a and b Interaction with Inner and Outer Surfaces of Single-Walled Carbon Nanotube Using Molecular Dynamics Simulation

M. Dehestani, M. Ghasemi-Kooch

Abstract—In this work, adsorption of chlorophylls a and b pigments in aqueous solution on the inner and outer surfaces of single-walled carbon nanotube (SWCNT) has been studied using molecular dynamics simulation. The linear interaction energy algorithm has been used to calculate the binding free energy. The results show that the adsorption of two pigments is fine on the both positions. Although there is the close similarity between these two pigments, their interaction with the nanotube is different. This result is useful to separate these pigments from one another. According to interaction energy between the pigments and carbon nanotube, interaction between these pigments-SWCNT on the inner surface is stronger than the outer surface. The interaction of SWCNT with chlorophylls phytol tail is stronger than the interaction of SWCNT with porphyrin ring of chlorophylls.

Keywords—Dynamic simulation, single walled carbon nanotube, chlorophyll, adsorption.

I. INTRODUCTION

CARBON nanotubes (CNTs) with many singular properties, such as unique mechanical, optical, electronic, structural and thermal properties [1]-[4] have gained recent attention in physical, biotechnological, and biomedical fields. Due to sp^2 hybridization of carbon in CNTs, they have a distinctive tendency to adsorb various molecules via the formation of π - π stacking, semi-hydrogen bonds [5], dative bonds, and hydrophobic effect. Several theoretical studies have been performed to investigate the interaction of CNTs with different molecules, such as amino acids [6], polycyclic aromatic hydrocarbons [7], DNA [8], drugs and surfactants [9]-[11].

The most important of green photosynthetic pigments are chlorophylls a and b. Their structures containing a porphyrin ring are shown in Fig. 1.

In this work, we investigate the interaction of chlorophylls a and b with inner and outer surfaces of SWCNT (15,15) using molecular dynamic simulation. This work provides a complete understanding of the interaction of the pigments with the nanotube and improvement of separation process of these pigments from each other.

M. Dehestani, is with the Chemistry Department, Shahid Bahonar University of Kerman, Kerman, Iran (corresponding author, phone: +98-34-31322106; fax: +98-34-31322100; e-mail: dehestani@uk.ac.ir).

M. Ghasemi-Kooch is with the Chemistry department, Shahid Bahonar University of Kerman, Kerman, Iran (e-mail: majid2012m@yahoo.com).

II. COMPUTATIONAL METHODS

For investigations of the adsorption of chlorophyll a (chl a) and chlorophyll b (chl b) pigments in aqueous solution on the inner and outer surfaces of SWCNT, we model four systems, as illustrated in Table I. Geometries are optimized using Gaussian-03 software package [12] to obtain the lowest energy ground state structures of these pigments. The (5,5) SWCNTs of length 5 nm generated using nanotube modeler. For all of systems, a $7 \times 4.5 \times 4.5$ nm³ simulation box which contains ~6655 water molecules was used. We used the Amber03 Force Field [13]. The LINear Constraint Solver (LINCS) algorithm [14] was applied to constrain all the equilibrium lengths used in the force field. Constant number of particles, volume, temperature (NVT) molecular dynamics simulations with periodic boundary conditions analysed performed using the GROMACS package 4.5.6 (<http://www.gromacs.org>) [15]. The NVT simulations at 300 K, using the V-Rescale coupling [16] were carried out for a total time of 10 ns with the first 300 ps used for temperature scaled equilibration.

TABLE I
DETAILS OF VARIOUS SYSTEMS SIMULATED IN THIS STUDY

No.	Pig name	Pig position	System name
1	chl a	in	chl a in
2	chl a	out	chl a out
3	chl b	in	chl b in
4	chl b	out	chl b out
5	chl a	no cnt	chl a free
6	chl b	no cnt	chl b free

III. RESULTS AND DISCUSSION

A. Equilibrium State and Lennard-Jones(L-J) Interactions of CNT and Pigments

Root-mean-square displacements (RMSDs) for chlorophylls a and b in the interior and outer of nanotube were calculated and results showed that the system was equilibrated for 1 ns at a constant temperature of 300 K. The LJ interaction energy pigments with nanotube and the number of contacts of atoms between pigments and nanotube are shown in Figs. 2 and 3. Contacts distance is 4 Å. As shown in Fig. 2, the interaction energy between pigments with the inner surface of nanotube is more negative than that with outer surface of nanotube. The reason of this strong interaction is the concavity of nanotube and the effect of the number of CNT atoms around the pigment. Fig. 3 shows that the number of contacts of pigments

atoms with nanotube atoms is more in inner surface than outer surface. Even though chl b is more polar than chla, interaction between chl b and nanotube in outer surface is weaker than that between chla and nanotube (Fig. 2). The presence of an aldehyde group in the chl b instead of a methyl group in chla

favors more atoms transfer of chl b from the surface of the nanotube to solvent mass and decreases interaction with nanotube surface. Interactions between nanotube and chla and chl b are almost the same in the inner surface.

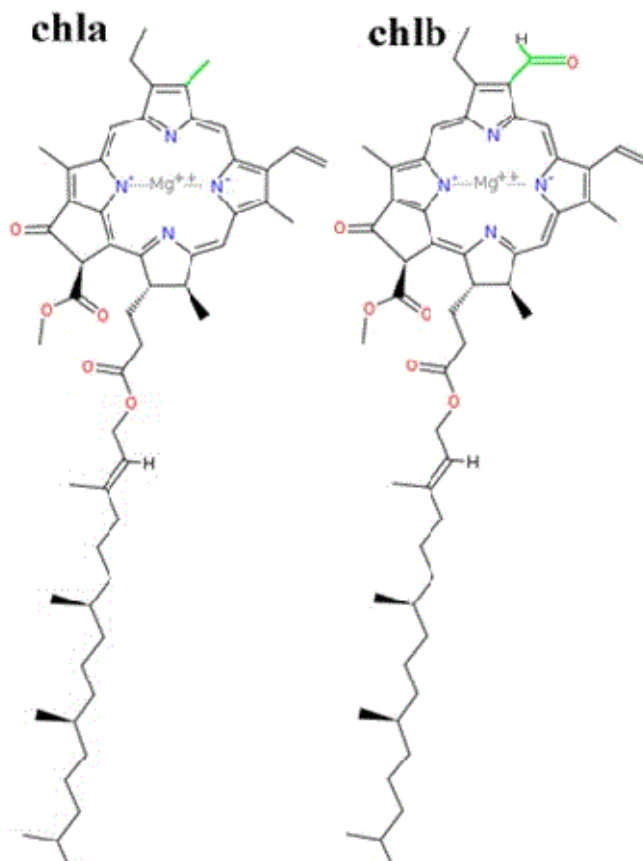


Fig. 1 Structure of Chlorophyll a and Chlorophyll b

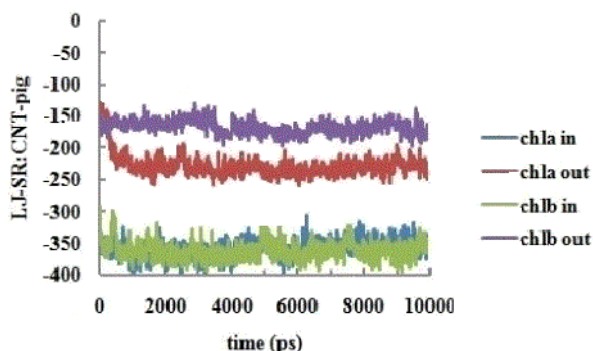


Fig. 2 The L-J energy between SWCNT and chlorophyll a and chlorophyll b pigments in kJ/mol

Comparing the two chlorophylls with each other, it is observed that the interaction of the outer surface of SWNT with chla is stronger than of the chl b. Although chl b is more polarized than the chla, but its interaction with SWCNT surface is less than chla because chl b has an aldehyde group instead of a methyl group of chla, that it makes more atoms transfer of chl b from the surface of the SWCNT to solvent

mass and reduces interaction with CNT surface. Fig. 2 depicts interaction energies of the inner surface of SWNT with chla and chl b having the same contact surface. Because of the small interior space of CNT in comparison to chlorophylls size for their, the number of connected atoms of both chlorophylls with SWCNT is the same.

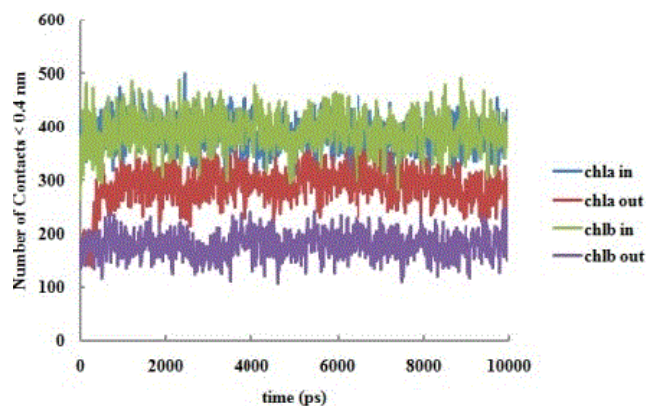


Fig. 3 Number of atomic contacts between pigment and CNT

B. Free Energy of Binding

Free energy of binding was calculated using the following equation [17]

$$G_{binding} = \alpha(V_{bond}^{el} - V_{free}^{el}) + \beta(V_{bond}^{vdW} - V_{free}^{vdW}) \quad (1)$$

where V_{bond}^{el} and V_{bond}^{vdW} are the electrostatic and van der Waals

interaction energies between pigment bonded to SWCNT with solvent and SWCNT (systems of 1 to 4 in Table I), respectively. V_{free}^{el} and V_{free}^{vdW} are the electrostatic and van der Waals interaction energies of pigment with solvent in systems that includes pigments and solvents (systems of 5 to 6 in Table I), respectively. Parameters α and β corresponding to experimental data are 0.5 and 0.16, respectively [18].

TABLE II
THE BINDING FREE ENERGY OF THE CNT-PIGMENT COMPLEXES

Pigment	Free		Position	Bonded		Free energy (kJ/mol)
	EL (kJ/mol)	VDW (kJ/mol)		EL (kJ/mol)	VDW (kJ/mol)	
chl a	-238.87	-246.87	In	-214.65	-513.96	-30.62
			out	-231.38	-459.15	-26.47
chl b	-265.07	-247.72	In	-244.08	-526.75	-34.15
			out	-249.57	-391.98	-15.33

TABLE III
INTERACTION ENERGY OF PIGMENT WITH CNT AND SOLVENT

Position	Pigment	Pig-cnt energy (kJ/mol)	Pig-sol energy (kJ/mol)	Pig-cnt – Pig-sol (kJ/mol)	Pig-cnt/Pig-sol (kJ/mol)
In	chl a	-356.16	-371.08	14.92	0.96
	chl b	-363.52	-408.09	44.57	0.89
Out	chl a	-231.39	-458.41	227.02	0.5
	chl b	-169.27	-476.87	307.60	0.35

Table II lists binding free energies of chlorophylls in both positions of inside and outside the nanotube. This energy is a negative value in both positions of CNT for chlorophylls a and b, which indicates thermodynamically favorable for adsorption of pigments in both positions of inside and outside the nanotube. Binding free energy for chlorophylls in position of inside the CNT is less than position of outside the CNT, so it is expected to be thermodynamically more favorable for adsorption of chlorophylls inside the nanotube. Because of the less L-J energy between chl b with the outer surface of CNT, difference between the binding free energies of chl a and chl b in the position of outside the CNT is big.

C. Comparison of Interaction Energy of Pigments with Solvent and Nanotubes

For investigation the separation chl a from chl b, one can use difference between interaction energy of chlorophyll pigments with solvent and SWCNT. Table III lists the interaction energy of chlorophyll pigments with solvent and CNT individually and the differences between these two values (column 5 of Table III) and ratio between the two energies (column 6 of Table III). Although the interaction of chlorophyll pigments with nanotube on the inner surface is stronger than of the outer surface, interaction of chlorophyll pigments with solvent molecules on the outer surface is stronger than that of the inner. The presence of a polar part (chlorin ring) and a non-polar (phytyl tail) in chlorophylls causes a greater tendency to interact with both solvent and CNT. The presence of a polar aldehyde group in the chl b compared to a methyl group in chl a causes its stronger interaction with water. By comparing difference between the calculated interaction energy values for two chlorophylls a and b with solvent and CNT (columns 5 & 6 of Table III) in the

outer surface with the inner surface, one expects to separate the two pigments with proper design of CNT, (closed CNT and CNT with small diameter) easily.

D. Locations of Pigments during the Simulation, and the Final Structure CNT

We plot the radial distribution function (RDF) for the chlorophylls toward the CNT. The first strong peak in plots occurs at short distances (< 0.5 nm) which shows that all pigments have a strong interaction with the surface of the nanotube at a distance of less than 0.5 nm.

IV. CONCLUSION

Chlorophylls a and b in aqueous solution are adsorbed on the surface of CNTs. The interaction energy between these pigments with CNT in the inner surface is stronger than that in the outer surface, and the pigments tend to be located inside the nanotube compared to the outer surface of the nanotube. Obviously, our results show that difference binding free energy between two positions of inside and outside of CNT surface for chl a compared to chl b is very small. The results demonstrate that the CNT is a strong candidate for pigments separation.

REFERENCES

- [1] B. I. Yakobson, P. Avouris, Mechanical properties of carbon nanotubes. In: Carbon nanotubes. 287-327. Springer, 2001.
- [2] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umez, S. Suzuki, Y. Ohtsuka, Y. Achiba: Optical properties of single-wall carbon nanotubes. Synthetic. Metals 103(1-3), 1999, pp. 2555-2558.
- [3] J. E. Fischer, A. T. Johnson, Electronic properties of carbon nanotubes. Curr. Opin. Solid State Mater. Sci. vol. 4(1), 1999, pp. 28-33.
- [4] J. Che, T. Cagin, W.A. Goddard III, Thermal conductivity of carbon nanotubes. Nanotechnology 11(2), 2000, pp. 65.
- [5] M. Levitt, M. F. Perutz, Aromatic rings act as hydrogen bond acceptors.

- J. Mol. Biol. 201(4), 1988, pp. 751-754.
- [6] S. Az'hari, Y. Ghayeb, Effect of chirality, length and diameter of carbon nanotubes on the adsorption of 20 amino acids: a molecular dynamics simulation study. *Mol. Simul.* Vol. 40(5), 2014, pp. 392-398.
- [7] R. P. Wesolowski, S. Furmaniak, A. P. Terzyk, P. A. Gauden, Simulating the effect of carbon nanotube curvature on adsorption of polycyclic aromatic hydrocarbons. *Adsorption* vol. 17(1), 2011, pp. 1-4.
- [8] M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. McLean, S. R., Lustig, R. E. Richardson, N. G. Tassi, DNA-assisted dispersion and separation of carbon nanotubes. *Nat. Mater.* Vol. 2(5), 2003, pp. 338-342.
- [9] B. S. Wong, S. L., Yoong, A. Jagusiak, T. Panczyk, H. K. Ho, W. H. Ang, G. Pastorin, Carbon nanotubes for delivery of small molecule drugs. *Adv. Drug Deliv. Rev.* vol. 65(15), 2013, pp. 1964-2015.
- [10] Z. Xu, X. Yang, Z. Yang, A molecular simulation probing of structure and interaction for supramolecular sodium dodecyl sulfate/single-wall carbon nanotube assemblies. *Nano Lett.* Vol. 10(3), 2010, pp. 985-991.
- [11] M. Ghasemi-Kooch, M. Dehestani, M. R. Housaindokht, M. R. Bozorgmehr, Oleuropein interactions with inner and outer surface of different types of carbon nanotubes: Insights from molecular dynamic simulation. *J. Mol. Liq.* vol. 241, 2017, pp. 367-373.
- [12] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, Gaussian 03, Revision B. 03. In: Gaussian, Inc., Wallingford CT, 2004.
- [13] Y. Duan, C. Wu, S. Chowdhury, M. C. Lee, G. Xiong, W. Zhang, R. Yang, P. Cieplak, R. Luo, T. Lee, A point-charge force field for molecular mechanics simulations of proteins based on condensed-phase quantum mechanical calculations. *J. Comput. Chem.* vol. 24(16), 2003, pp. 1999-2012.
- [14] B. Hess, H. Bekker, H. J. C. Berendsen, J. G. E. M. Fraaije, LINCS: A linear constraint solver for molecular simulations, *J. Comput. Chem.* vol. 18(12), 1997, 1463-1472.
- [15] M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess, E. Lindahl: GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *Software X* 1, 2015, pp. 19-25.
- [16] G. Bussi, D. Donadio, M. Parrinello, Canonical sampling through velocity rescaling. *J. Chem. Phys.* vol. 126(1), 2007, pp. 014101.
- [17] J. Åqvist, C. Medina, J.-E. Samuelsson, A new method for predicting binding affinity in computer-aided drug design. *Protein Eng.* vol. 7(3), 1994, pp. 385-391.
- [18] W. Wang, J. Wang, P.A. Kollman, What determines the van der waals coefficient β in the LIE (linear interaction energy) method to estimate binding free energies using molecular dynamics simulations? *Proteins: Struct. Funct. Bioinf.* vol. 34 (3), 1999, pp. 395-402.