Understanding the Spectroscopic Properties of the Photosynthetic Reaction Center of *Rhodobacter sphaeroides* by a Combined Theoretical Study of Absorption and Circular Dichroism Spectra

Yanliang Ren[†], Wei Ke[†], Yongjian Li[†], Lingling Feng[†], Jian Wan[†,], Xin Xu[‡,*]*

[†]*Key Laboratory of Pesticide & Chemical Biology (CCNU), Ministry of Education and Department of Chemistry, Central China Normal University, Wuhan 430079, China*

[‡]*State Key Laboratory for Physical Chemistry of Solid Surfaces; College for Chemistry and Chemical Engineering, Center for Theoretical Chemistry, Xiamen University, Xiamen 361005, China*

SUPPORING INFORMATION

Computational details

The initial geometric parameters of Models I and II were built up in terms of a data set of the crystal structure of *Rb. sphaeroides*[1] (PDB ID: 1PCR). The hydrogen atoms were added by Gaussview 3.07[2] and subsequently optimized by using the PM3[3] method implemented in Gaussian 03 program package.

Model I was a reduced super molecular cluster model of the prosthetic groups, including P, B_M, B_L, H_M and H_L chromophore (see Figure 1). Model II was a simplified individual chromophore model (see Figure S1).

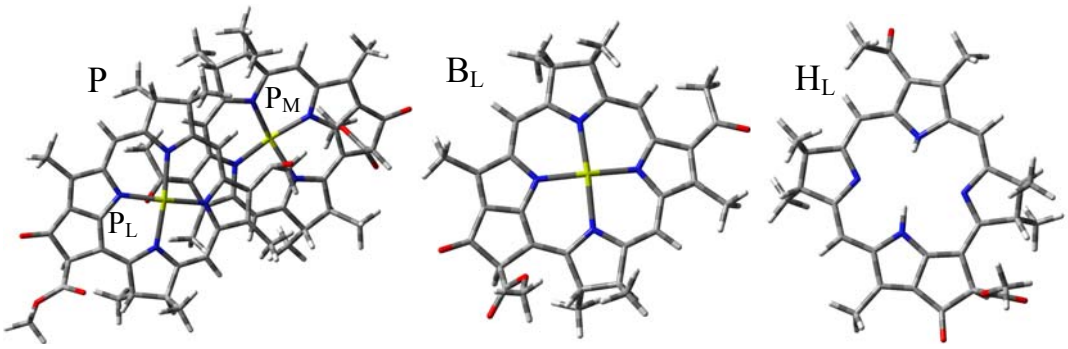


Figure S1. Schematic of the individual chromophore model of PSRC from *Rb. sphaeroides*. The reduced rules for the M-branch chromophores are the same as those for the L-branch ones.

The low-lying singlet electronic excited states of the prosthetic groups in PRSC from *Rb. sphaeroides* calculated at two chemistry models. The excitation energies, oscillator strengths (>0.1) and rotational strengths for two models were shown in Tables S1 and S2, respectively.

Table S1. The excited states of model I for PSRC from *Rb. sphaeroides* calculated at B3LYP/6-31G level

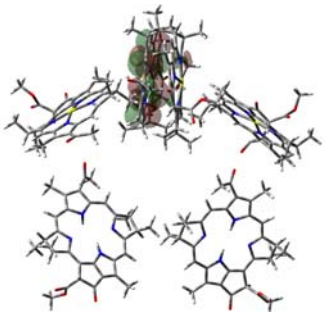
Chro.[a]	States	Main Config.[b] (|c| > 0.3)	$E_{ex.}$[c]	Osc.[d]	$R^e(10^{-40}$cgs)	Exptl.[4]	
						E_{ex} (eV)	CD Peak
$P_M \rightarrow P^*_M$	14^1A	-0.53 (877→883)	1.717	0.421	302.0	1.45	i
$P_L \rightarrow P^*_M$	18^1A	-0.56 (875→883)	1.819	0.154	-64.3	1.53	ii
$B_M \rightarrow B^*_M$ $P_L \rightarrow B^*_M$	19^1A	+0.33(882→888) -0.31(880→888)	1.863	0.222	-1021.0	1.53	ii
$B_L \rightarrow B^*_L$ $P_L \rightarrow B^*_M$	20^1A	-0.37(881→886) -0.34(880→888)	1.871	0.464	848.9	1.54	iii
$P_L \rightarrow B^*_M$ $B_M \rightarrow B^*_M$	21^1A	+0.53(880→888) +0.33(882→888)	1.877	0.285	497.5	1.54	iii
$P_M \rightarrow P^*_L$	25^1A	+0.49(877→887)	1.947	0.147	234.1	1.54	iii
$H_L \rightarrow H^*_L$	26^1A	+0.51(878→884)	1.955	0.209	-252.3	1.66	iv
$H_M \rightarrow H^*_M$	27^1A	+0.57(879→885) +0.32(874→891)	1.959	0.205	-203.1	1.66	iv

[a]Chromophore. [b]main configuration [c]Excitation energy in eV. [d]Oscillator strength in a. u. [e]Rotatory Strengths.

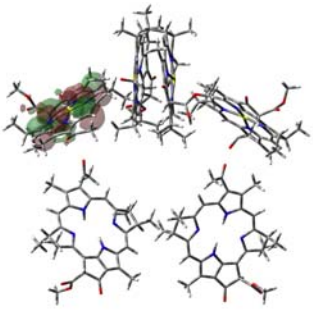
Table S2. The excited states of model II for PSRC from *Rb. sphaeroides* calculated at B3LYP/6-31G level.

		B3LYP/6-31G				Exptl.[4]
Chro.[a]	States	Main Config.[b] (|c| > 0.3)	$E_{ex.}$[c]	Osc.[d]	R^e (10^{-40}cgs)	CD Peak
$P_M \rightarrow P^*_M$	2^1A	0.52(299→301)	1.729	0.330	163.0	i
$P_L \rightarrow P^*_M$	3^1A	0.59 (298→301)	1.822	0.121	-28.5	ii
$B_M \rightarrow B^*_M$	1^1A	0.58(148→149)	1.895	0.370	-7.0	ii
$B_L \rightarrow B^*_L$	1^1A	0.58(148→149)	1.895	0.358	8.3	iii
$H_L \rightarrow H^*_L$	1^1A	0.31(142→145) +0.59(143→144)	1.952	0.293	-0.1	iv
$H_M \rightarrow H^*_M$	1^1A	0.33(142→145) +0.59(143→144)	1.957	0.236	-6.4	iv

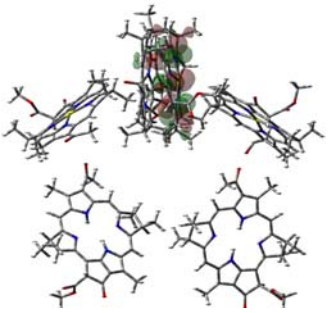
[a]Chromophore. [b]main configuration [c] Excitation energy in eV. [d]Oscillator strength in a. u. [e]Rotatory Strengths.



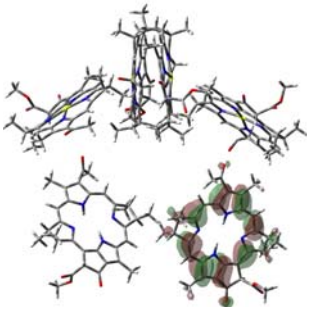
MO-875



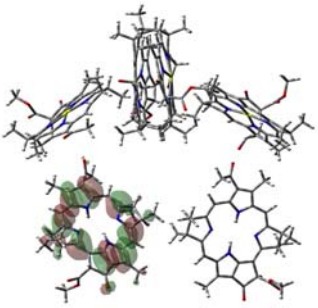
MO-876



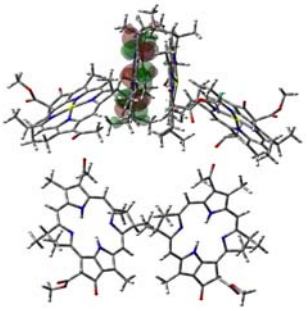
MO- 877



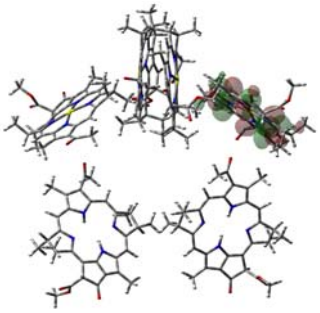
MO-878



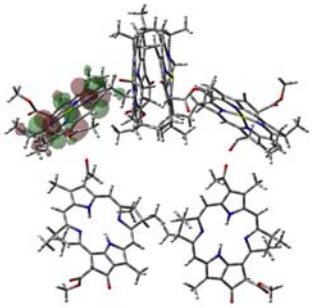
MO-879



MO-880

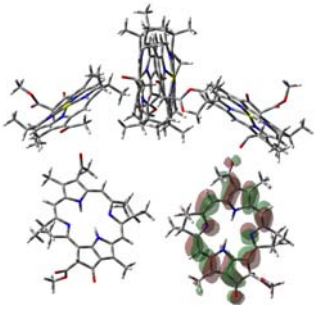


MO-881

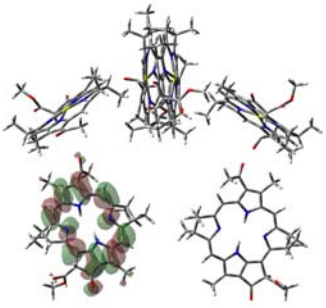


MO-882 (HOMO)

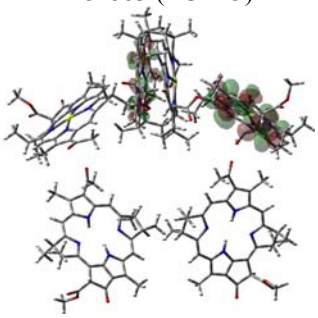
MO-883 (LUMO)



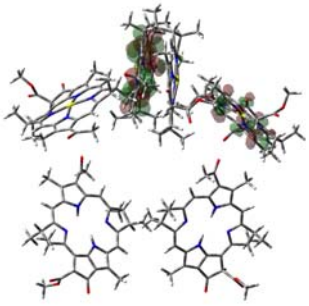
MO-884

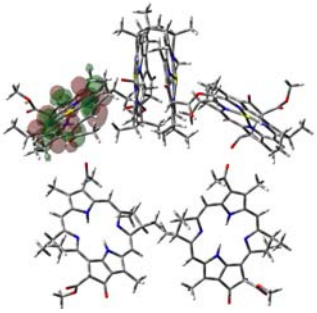


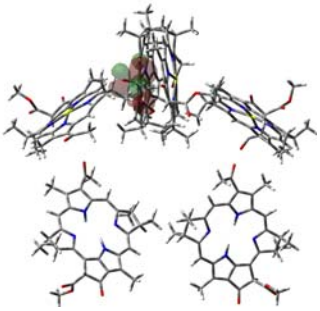
MO-885



MO-886







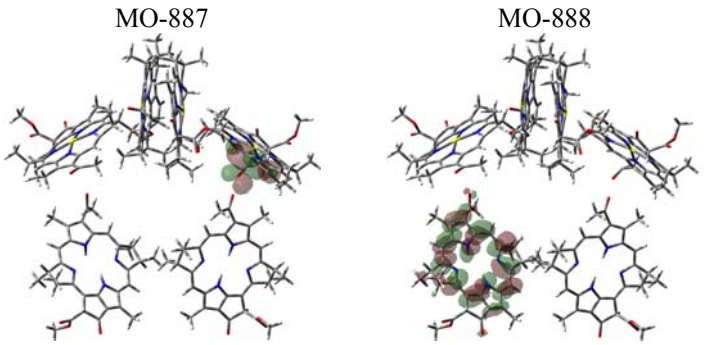


Figure S2. Contour maps of some important molecular orbitals for Model I calculated at B3LYP/6-31G level.

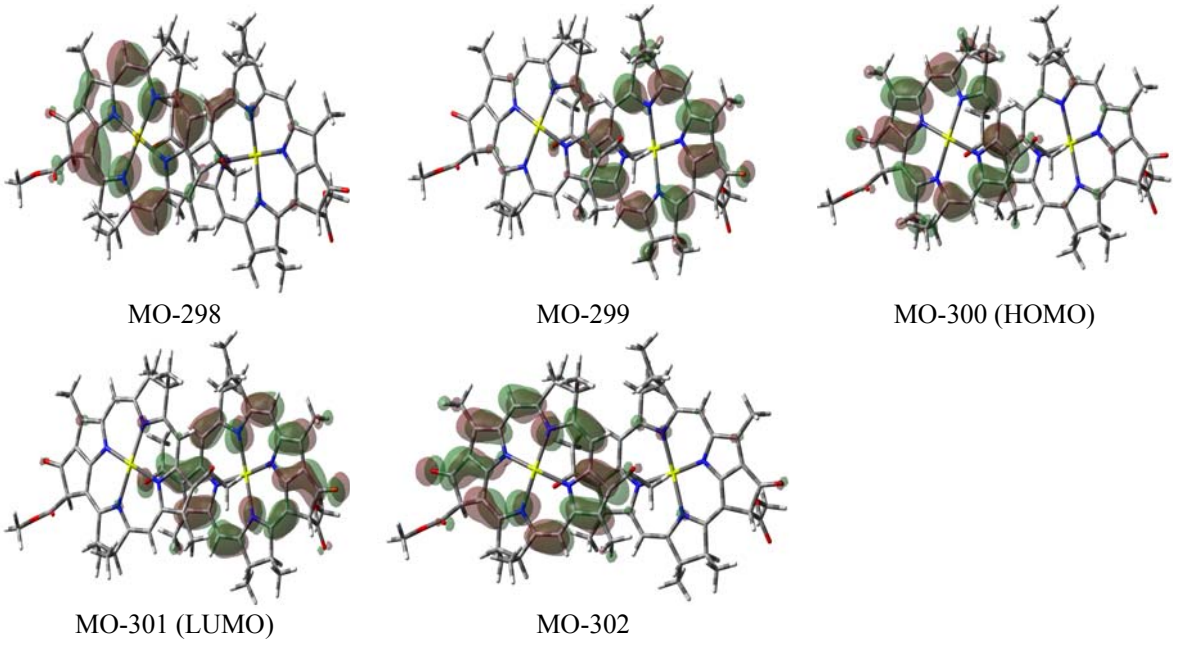


Figure S3. Contour maps of some important molecular orbitals of P chromophore for Model II calculated at B3LYP/6-31G level.

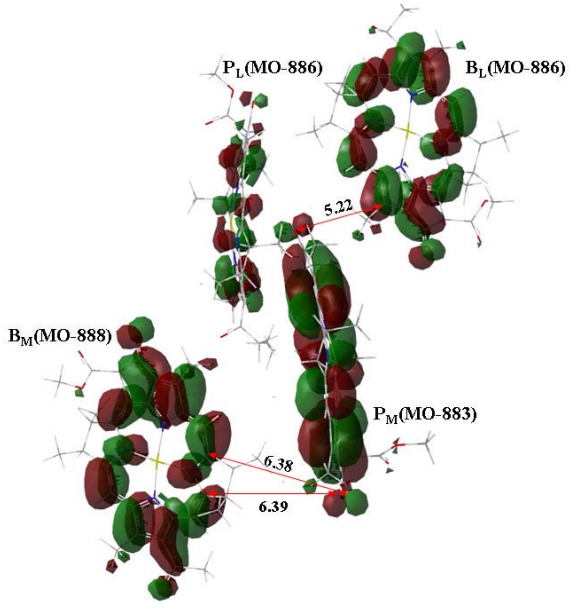


Figure S4. Schematic for the resultant unoccupied MOs of 883, 886, and 888 in Model I.

References

1. Ermler, U.; Fritzsch, G.; Buchanan, S. K.; Michel, H. *Structure*. **1994**, *2*, 925-936.

2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T. Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. (Revision D.01), Gaussian, Inc., Pittsburgh PA (2004).

3. Stewart, J. J. P. *J. Comp. Chem*, **1989,** *10*, 209-220.

4. Reed, D. W.; Ke, B. *J. Biol. Chem.* **1973**, *248*, 3041-3045.