Electronic Supplementary Information

On the Dimerization of Chlorophyll in Photosystem II

Sten O. Nilsson Lill*

Table S1. B3LYP-DCP optimized and experimentally determined[1,2] (in parenthesis) nitrogen-magnesium distances (in Å)

	Mg_{D1}	Mg_{D2}
N_I(pyrrole)	2.047 (2.091[1]/2.018[2])	2.044 (2.096[1]/2.022[2])
N_{II}(pyrrole)	2.096 (2.129/2.153)	2.081 (2.118/2.145)
N_{III}(pyrrole)	2.042 (2.031/2.022)	2.036 (2.051/1.993)
N_{IV}(pyrrole)	2.166 (2.137/2.238)	2.149 (2.122/2.235)
N(histidine)	2.156 (2.240/2.233)	2.175 (2.220/2.180)
Vinyl C=C	3.529 (3.936/4.394) 4.384 (4.882/5.216)	3.206 (2.718/3.430) 3.268 (3.868/3.841)

1 B. Loll, J. Kern, W. Saenger, A. Zouni, A. and J. Biesiadka. *Nature*, 2005, **438**, 1040-1044.
2 Y. Umena, K. Kawakami, J.-R. Shen, and N. Kamiya. *Nature*, 2011, **473**, 55-61

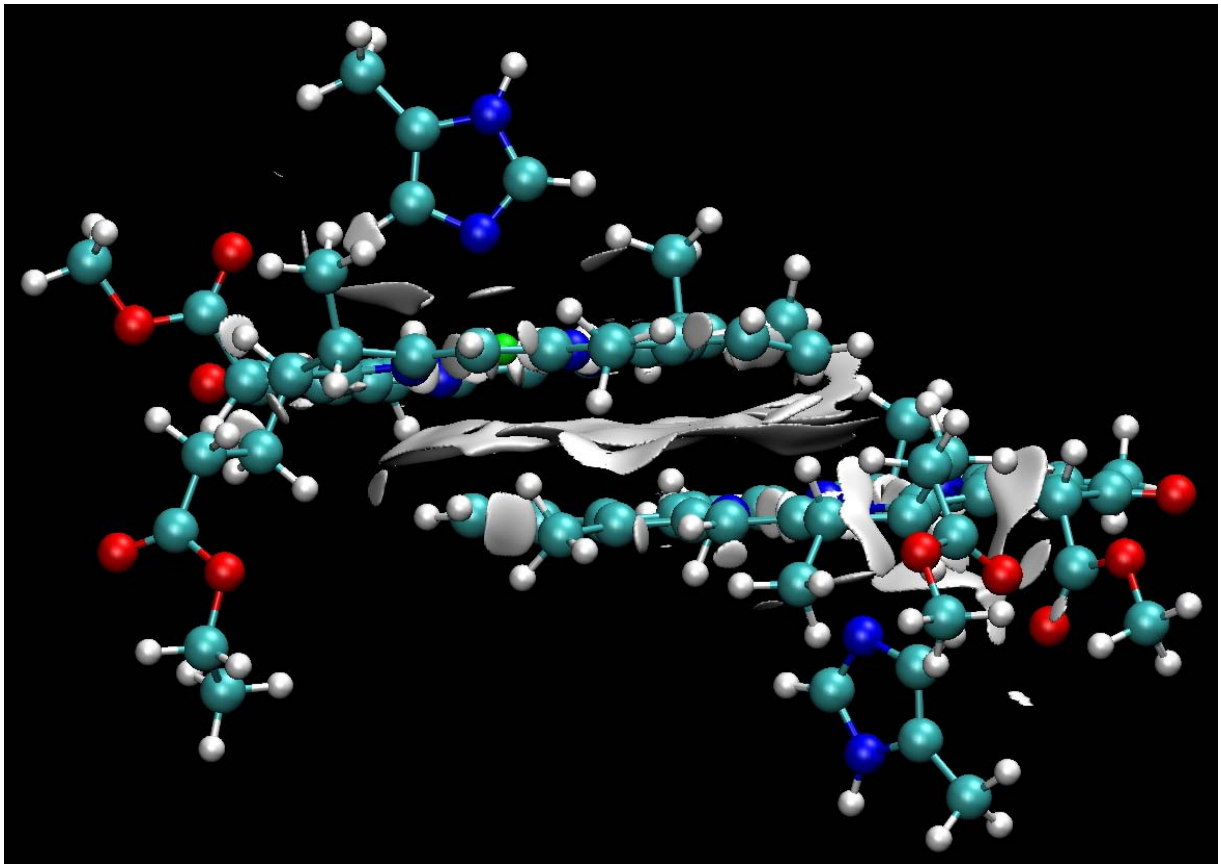

Figure S1. Sideview of non-covalent interactions (NCI) plot of the B3LYP-DCP optimized chlorophyll dimer illustrating the region of overlap between the porphyrin rings. Isosurface of reduced density gradient set to 0.3.

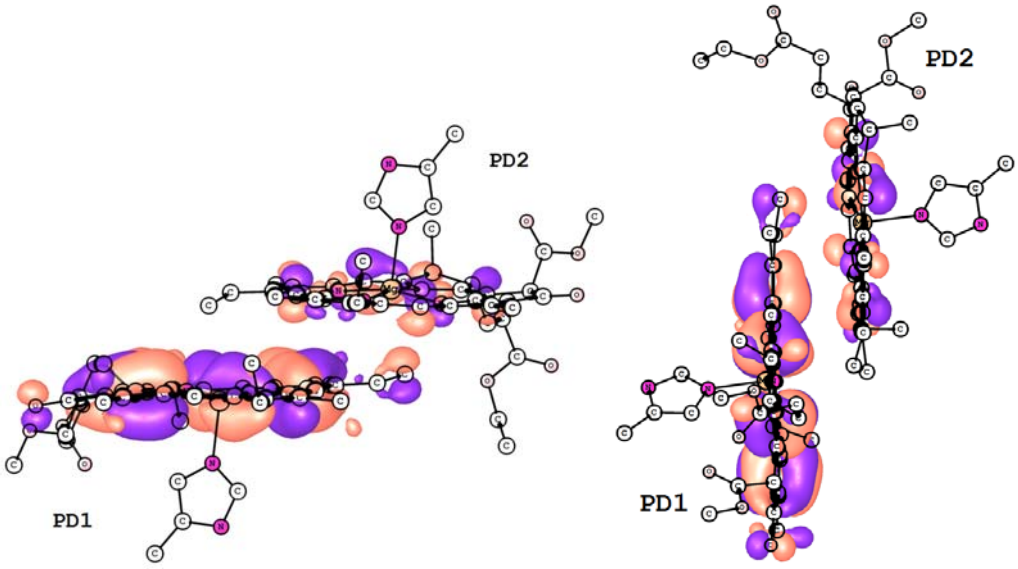

Figure S2. Sideview of the HOMO of the B3LYP-DCP optimized chlorophyll dimer.

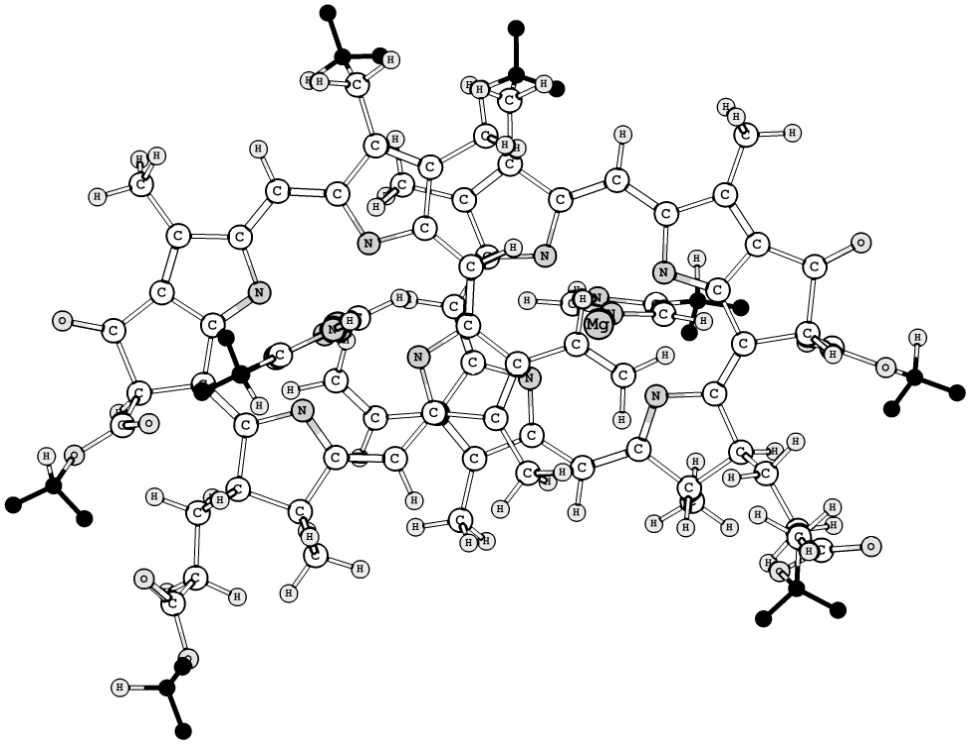

Figure S3. Structure of the chlorophyll dimer. Atoms marked in black were initially held fixed in the position taken from the X-ray structures.

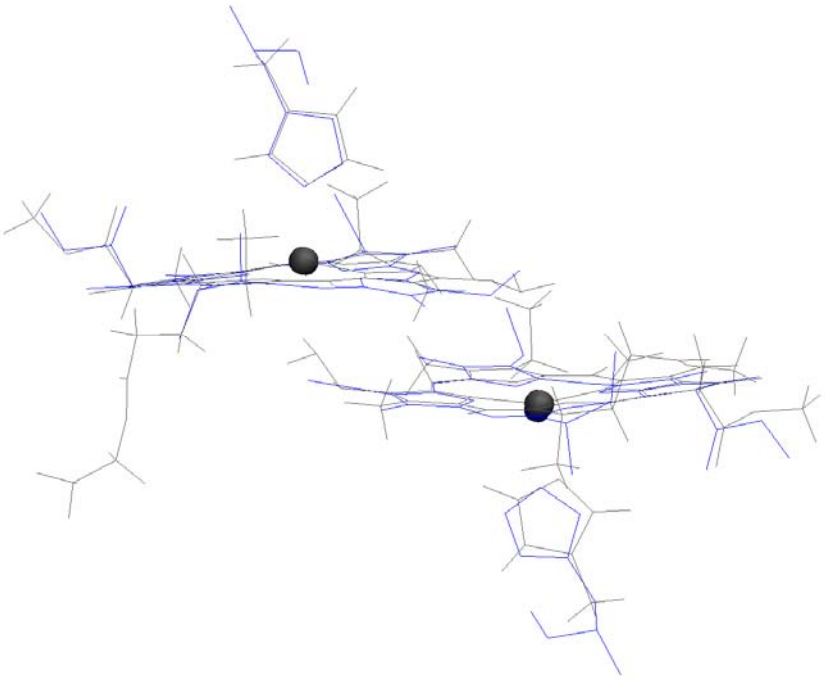

Figure S4. Sideview of the overlay of crystal structure (red, 3.0 Å) used in the present study with the more recent crystal structure (blue, 1.9 Å).

Cartesian coordinates of B3LYP-DCP optimized chlorophyll dimer:

6	-7.255151000	-0.621957000	4.853430000
6	-6.026896000	-0.149263000	4.157090000
7	-4.904309000	0.330483000	4.814266000
6	-5.717127000	-0.069127000	2.825583000
6	-3.979514000	0.675922000	3.878712000
7	-4.442666000	0.444383000	2.666576000
1	-7.982156000	-0.951682000	4.107656000
1	-7.719977000	0.172536000	5.450256000
1	-4.790345000	0.413055000	5.813705000
1	-6.342277000	-0.350495000	1.991336000
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6	7.193564000	1.675005000	-5.119054000
6	5.924611000	1.545225000	-4.350795000
7	4.672991000	1.808509000	-4.885595000
6	5.682883000	1.177609000	-3.053271000
6	3.743677000	1.595700000	-3.914384000
7	4.325245000	1.213589000	-2.795915000
1	8.031909000	1.402053000	-4.473953000
1	7.358607000	2.701697000	-5.468732000
1	4.480765000	2.108935000	-5.829771000
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Full reference for Gaussian 03, ref. 32

Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, 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.; and Pople, J. A. Gaussian 03, Revision D.02, (Gaussian Inc., Wallingford, CT, 2004).