Measure of Complexity in Artificial Minimal Cells

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The nano-protoorganisms that are proposed in [1] are only a few nm in size. The minimal protocell contains on the order of 10^3 atoms.

Due to its small size, the entire protocell might be considered to be a molecular electronics device that self-assembles according to quantum-based electron interaction potentials and that absorbs light and carries on its metabolism according to quantum mechanical (QM) electron excitation and tunnelling equations [2].

[1] S. Rasmussen, L. Chen, M. Nilsson, and S. Abe, *Artificial Life*, vol 9, 267-316, 2003.

[2] A. Tamulis, V. Tamulis A. Graja; *Journal of Nanoscience and Nanotechnology*, vol. 6, 965-973, 2006.

In their simplest form, these protoorganisms consist of a micelle which acts as the container, a light driven metabolism, and a genetic system.

The container consists of amphiphilic fatty acid (FA) molecules that self-assemble into a micelle. The hydrophobic interior of the micelle provides an alternative thermodynamic environment from the aqueous exterior and acts as a sticking point for the photosensitizer, fatty acid precursors (pFA) (food), and the genetic material. Peptide nucleic acid (PNA) is chosen as the genetic material as it is far less polar than RNA or DNA and therefore should stick to the micelle [3, 4].

[3] S. Rasmussen, J. Bailey, J. Boncella, L. Chen, G. Collins, S. Colgate, M. DeClue, H. Fellermann, G. Goranovic, Y. Jiang, C. Knutson, P.-A. Monnard, F. Moufouk, P. Nielsen, A. Sen, A. Shreve, A. Tamulis, B. Travis, P. Weronski, W. Woodruff, J. Zhang, X. Zhou, and H. Ziock, "Assembly of a minimal protocell", to be published in MIT Press book, "Protocells: Bridging nonliving and living matter", eds S. Rasmussen, M. Bedau, L. Chen, D. Krakauer, D. Deamer, N. Packard, and P. Stadler, 2007.

[4] A. Tamulis, V. Tamulis, H. Ziock, S. Rasmussen, "Influence of Water and Fatty Acid Molecules on Quantum Photoinduced Electron Tunnelling in Photosynthetic Systems of PNA Based Self-Assembled Protocells", printing process in "Multi-scale Simulation Methods for Materials", eds. R. Ross and S. Mohanty, John Wiley & Sons, Inc., New Jersey, 2006.

Some of the main parts of one of the artificial minimal cell proposed in [1] include a PNA double helix molecule which is covalently bonded to the 1,4-bis(N,N-dimethyl-amino)naphthalene sensitizer molecule shown at bottom centre, a pFA molecule (bottom right), an SH anion molecule (centre left). Carbon atoms are shown as grey spheres, hydrogens are blue, oxygens – red, nitrogens – green, sulphur – gold. Quantum self-assembly was done by QM density functional (DFT) methods in the GAMESS-US package.

The most intense absorption line in vacuum as calculated using the time dependent (TD) DFT *Perdew, J. P., Burke, K. & Ernzerhof, M. (1996) Phys. Rev. Lett. 77, 3865-3868* (PBEPBE) model using the 6-31G basis set is at 355 nm [4].

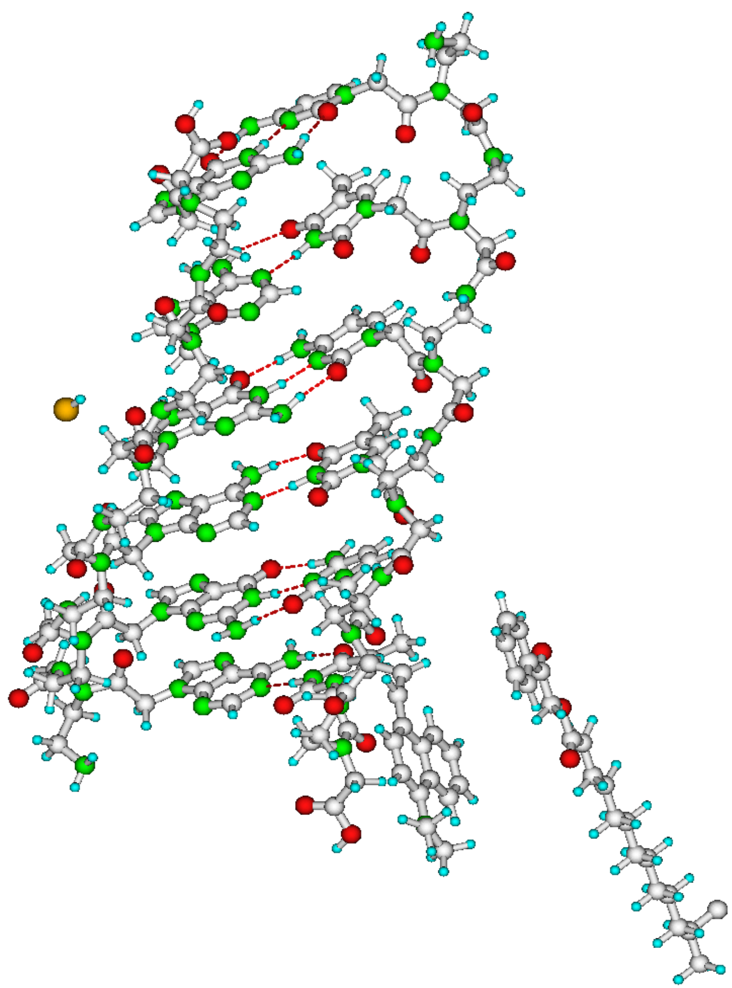


Image of the geometric and electronic structure of a cytosine-PNA fragment which is covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule in a system that also includes a pFA molecule and a number of water molecules, whose positions were optimized using the DFT PBEPBE/6-31G model. The water molecules organized to nano ice-like substructures.

The most intense absorption line was calculated using the TD DFT PBEPBE/6-31G in conjunction *with the water cavity shell IEFPCM solvent model* is at 425.91 nm [4]. *The IEFPCM model is based on the work of Cances E, Mennucci B., Journal of Chemical Physics 2001;114(10):4744-4745* .

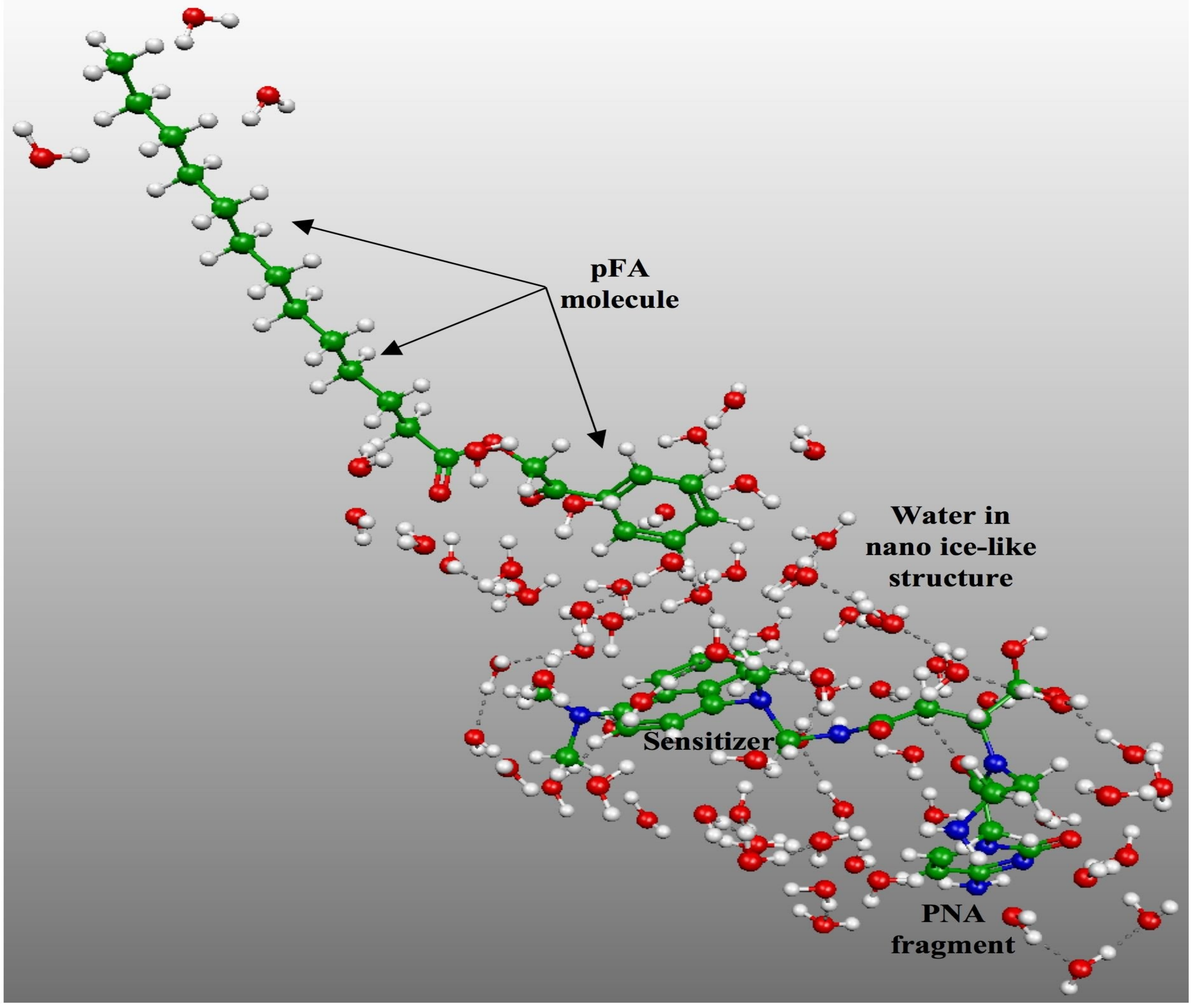
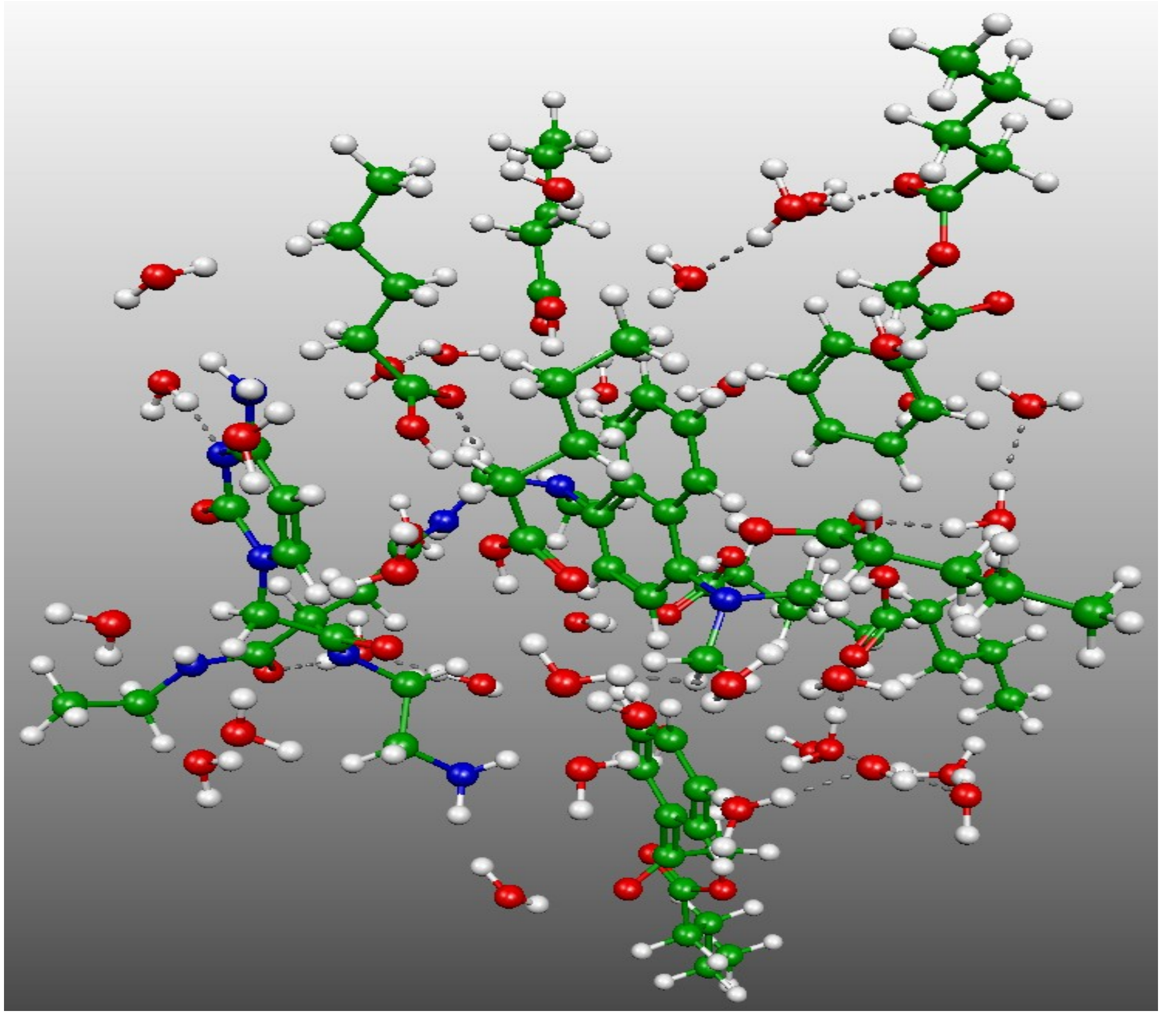
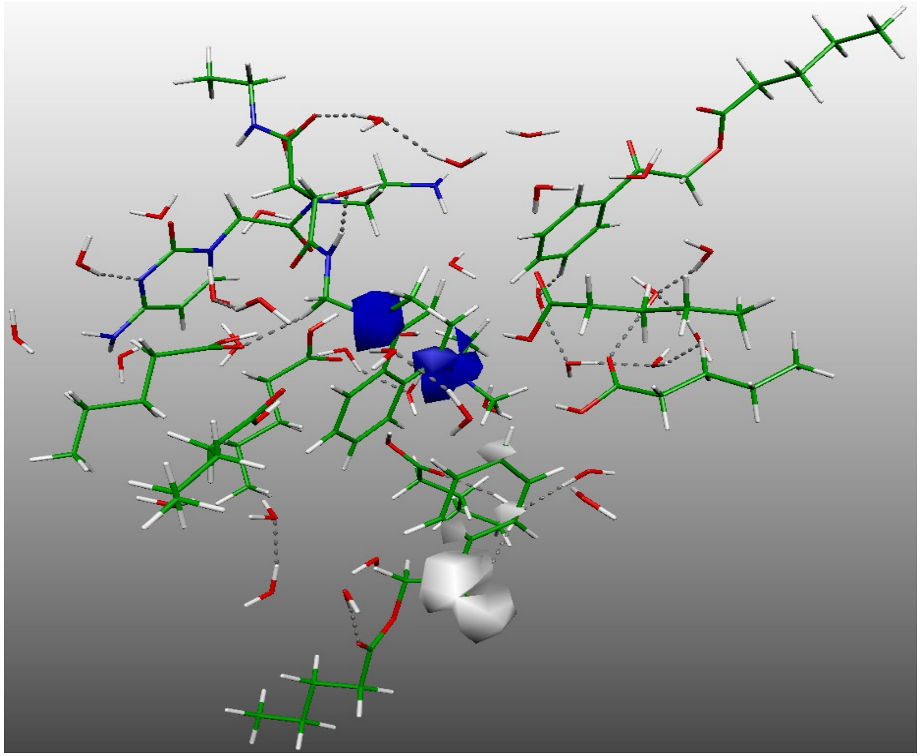


Image of the geometric and electronic structure of a quantum mechanically self-assembled photosynthetic system consisting of a cytosine-PNA fragment covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule (in the centre), two pFA molecules (bottom and top-right), six FA molecules, and water molecules that were optimized using the QM DFT PBEPBE/6-31G method. The water molecules organized into nano ice-like substructures. Carbon atoms and their associated covalent bonds are shown as green spheres and sticks, hydrogens are in grey, oxygens – red, nitrogens – blue. Hydrogen bonds are depicted by dashed lines. This is our most complete model of this photosynthetic system and includes the micellar container's inner (internal) monolayer surrounded by water molecules and was used to calculate electron transfers for excited states.



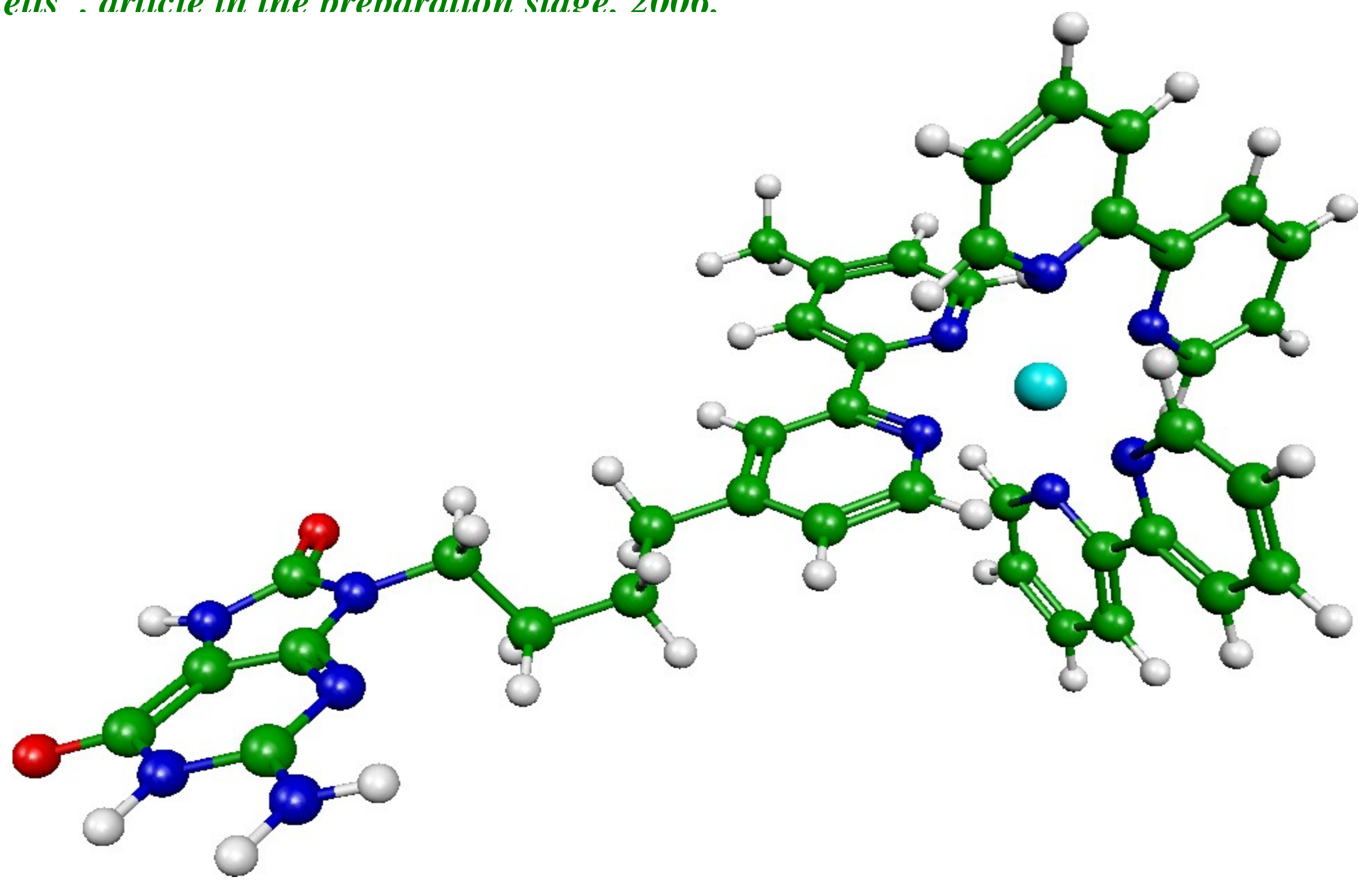
Visualization of the electron charge tunnelling associated with the most intense excited state was done using the QM TD DFT PBEPBE model with the 6-31G basis set. The electron cloud hole is indicated by the blue colour while the transferred electron cloud location is visualized by the grey colour. The calculation indicated that the most intense electron charge transition from the 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule to one of the pFA molecules (in bottom) was for the ninth excited state and had an energy and wavelength of 2.818 eV and 440.0 nm respectively. 10 nm shift to blue in comparison with the experimental value of 450 nm [3] is possible to understand as being due to the greater number of water and FA molecules found in the real system.

One notes that the calculated absorption lines for all the previous models (most intense lines: 355.0 nm – in vacuum, 425.91 nm - in water cavity, and 440.0 nm in our last and most complete model) are all shifted to the blue when compared with the experimental value of 450 nm. However, one also notes that as the complexity of the model is increased, the line value moves to red ever closer to the experimental value. The addition of evermore water and FA molecules results in smaller gaps between the ground and excited state energy levels. The real system ("having" the most water and FA molecules) has the smallest gap between the ground and excited states. The vacuum model case (i.e., no water) as expected has the largest gap and hence shortest wavelength associated with it.

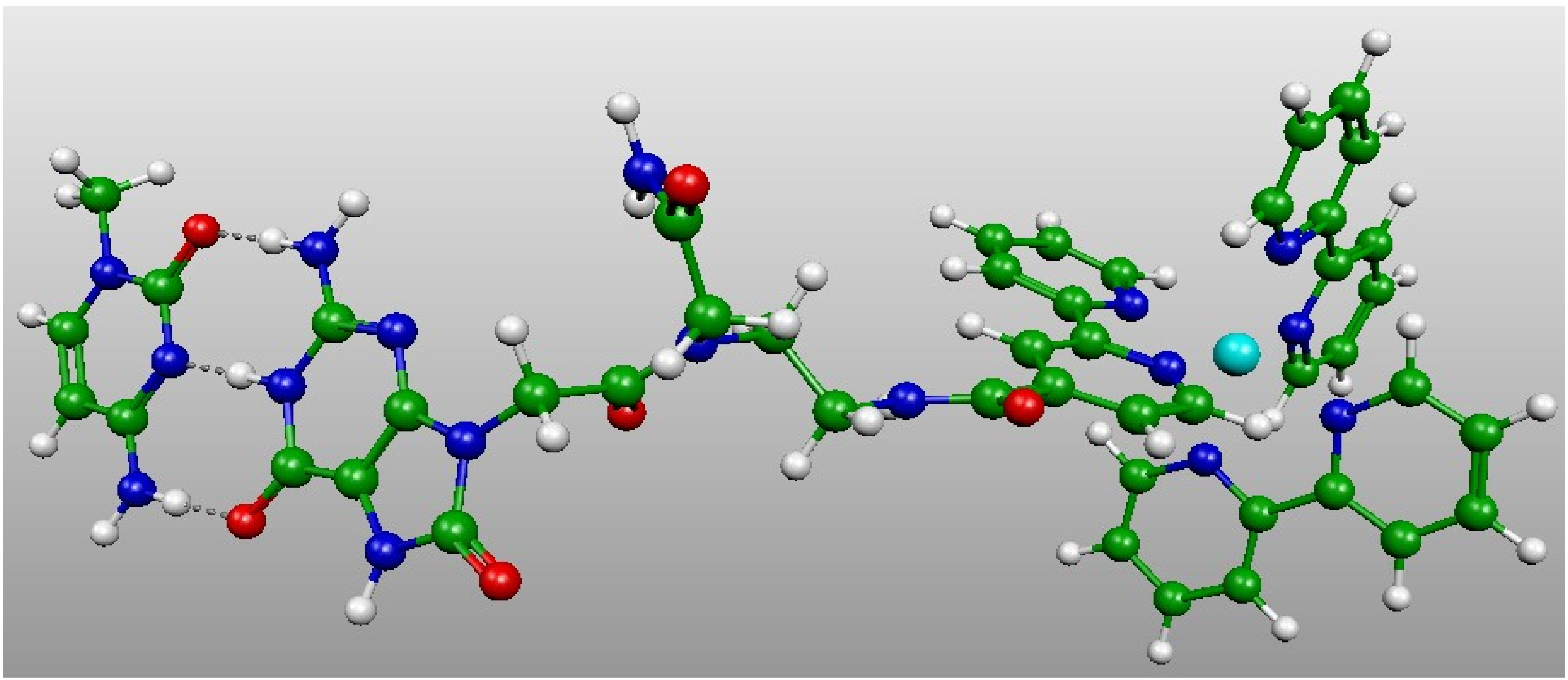


We have done quantum mechanical geometry optimization of a new more effective and more complex photosynthetic system composed of a Ru(bipyridine)$_3^{2+}$ sensitizer covalently bonded to an 8-oxo-guanine [3, 5] plus two pFA using Becke's 3 parameter exchange functional with non-local Lee-Yang-Parr electron correlations (B3LYP) together with the methanol cavity shell IEFPCM solvent model and the LanL2DZ basis set. The most intense singlet-singlet electron charge transfers for this supermolecule 8-oxo-guanine-Ru(bipyridine)$_3^{2+}$ are found for the regions: from 401.96 nm (less intense) to 433.54 nm (most intense) and 437.20 nm, and from 447.33 nm (more intense) to 464.10 nm. Experimental values of bands with maximal Gaussians are centred at 425.6 nm and 459.1 nm.

[5] A. Tamulis, V. Tamulis, S. Rasmussen, J. A. Bailey, H. Ziock, "Quantum Processes in Photosynthetic Systems of Artificial Minimal Cells", article in the preparation stage, 2006.



To investigate the likely impact of using a double-stranded genetic system, we also studied the above system with a PNA single strand involving an 8-oxo-guanine but with a cytosine hydrogen bonded to it in a water solvent. This system is shown below. The result of the hydrogen bonded cytosine molecule is a shift of the lowest prominent (6^{th}) excited state wavelength from 455.18 nm to 456.99 nm, i.e. 1.81 nm to the red. This behaviour matches what is experimentally seen for such an interaction; namely a splitting of the spectra for complex quantum systems due to such hydrogen bonding interactions with an additional molecule [5].



SUMMARY

The quantum mechanical model of the photosynthetic system of a minimal cell possessing 1,4-bis(N,N-dimethylamino)naphthalene sensitizer gave a wavelength of 440.0 nm for the most strongly absorbed excitation photon, which compares well with the experimental value of 450.0 nm [3, 4] of a real minimal cell that has more molecules than we modelled in paper [4].

We performed time dependent quantum mechanical investigations of a photosynthetic system consisting of good sensitizer Ru(bipyridine)$_3^{2+}$ working under excitation by visible light in the region from 455.18 nm to 402.85 nm and relaxing due to the passing of an electron from a good electron donor (8-oxo-guanine) via a PNA molecule bridge in a water solvent.

The influence of a hydrogen bonded cytosine molecule to the 8-oxo-guanine system resulted in a shift of the lowest intense excited state wavelength from 455.18 nm to 456.99 nm, *i.e.* 1.81 nm to the red. This is the usual process of the splitting of the spectrum of a complex quantum system due to a hydrogen bonding interaction with an additional molecule.

The inclusion of ever more water, fatty acid and nucleobase molecules in the different models results in a shift of the absorption spectrum to the red for the artificial protocell photosynthetic centre, leading to an ever closer approach to the real experimental value and indicates the measure of the complexity of this quantum complex system, *i.e. a* minimal protocell.

Acknowledgements

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