Oral Contributions

[MS31] Photocrystallography
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[MS31 - 01] Towards Biophotocrystallography with Photooxidisable Ruthenium Polypyridyl Complexes Christine J. Cardin and James P. Hall.

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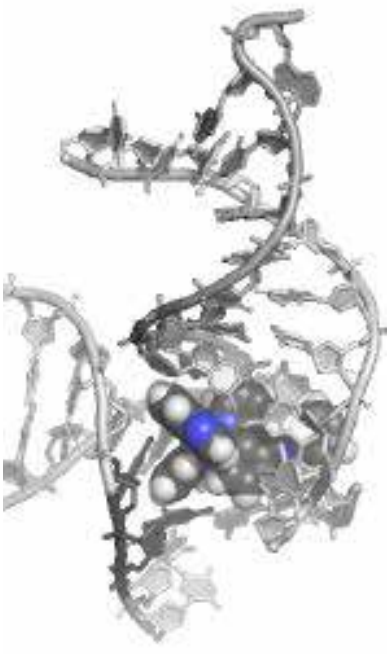
The earliest steps in DNA photodamage are of fundamental importance for an understanding of both the creation of potentially cancer-inducing DNA lesions and of damage repair by photodynamic therapy. It is well established that the DNA base guanine is the most susceptible of the four bases, and that –GG- is a more susceptible sequence than a single G, with 8-oxoguanine the best known oxidation product. The formation of 8-oxoguanine leads to subsequent base mismatching and copying errors.



We recently determined the static structure of the photooxidising complex -$[Ru(TAP)_2dppz]^{2+}$ (1) (TAP = tetraazaphenanthren Halogen Bonding and Solid Solution. Maciej Kubickia, Agnieszka Poulaina,b,c, Claude Lecomteb. e; dppz = dipyridophenazine) bound to the DNA duplex $d(TCGGCGCCGA)^2$ [1]. The structure showed the dppz ligand intercalated at the terminal step, with one TAP ligand semi-intercalated at the GG step of an adjacent duplex. A kink of about 50 ° is introduced at the semi-intercalation step. The combination of these two interactions generates a crystal lattice which suggests great potential for a photocrystallographic study of the excited state. Ultrafast laser solution studies of 1 with natural DNA or with $d(CG)_n$ polymer showed that electron transfer (possibly proton –coupled) occurs with a lifetime of 500 ps, yielding one-electron oxidised guanine [2]. Recent preliminary data on the observation of similar transients in the crystal lattice will be presented.

1. Hall, J. P.; O'Sullivan, K.; Naseer, A.; Smith, J.A.; Kelly, J.M.; Cardin, C.J. *Proc. Natl. Acad. Sci. USA,* **2011**, 108, 1761–17614.

2. Elias, B.; Creely C.; Doorley G. W.; Feeney M. M.; Moucheron C.; Kirsch - De Mesmaeker A.; Dyer J.; Grills D. C.; George, M.W.; Matousek, P.; Parker, A. W.; Towrie, M.; Kelly, J.M. *Chemistry – Eur. J,* **2008**, 14, 369-375.

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