Generation of Thymine Triplet State by Through-Bond Energy Transfer

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Direct or indirect absorption of UV radiation by DNA bases induces photochemical reactions damaging the genetic code. Thymine (Thy) pyrimidine dimers are the main photoproducts generated via both mechanisms.\textsuperscript{[1]} In this context, drugs containing the benzophenone (BP) chromophore, have been reported as DNA photosensitizers (PS) via triplet-triplet energy transfer (TTET),\textsuperscript{[2]} although surprisingly, direct evidence of the key species $3^\text{Thy}^*$ upon BP photosensitization has never been provided.

In the present work, direct spectroscopic fingerprint for the formation of $3^\text{Thy}^*$ through-bond (TB) TTET from $3^\text{BP}^*$ is provided. This goal has been achieved in two new systems that have been designed and synthesized with one BP and one Thy covalently linked to both ends of the rigid skeleton of the natural bile acids cholic or lithocholic acid. The transient absorption spectra of these two systems were recorded upon excitation of the BP and clear differences were noticed in the region between 350 and 400 nm compared to the single BP molecule, accompanied with a shorter lifetime of $3^\text{BP}^*$, which was consistent with the presence of $3^\text{Thy}^*$, that would result from TB-TTET (see figure below). The results shown here prove that it is possible to achieve triplet energy transfer to a Thy unit even when the PS is at a long (non-bonding) distance.

References