

**Ground and Triplet State Properties of a Dendritic methano[60]fullerene Octadeca-acid in Water and of its Tert-butyl ester in Organic Solvents: Evidence for Aggregation of the Acid Form in Water**

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The results of a laser flash photolysis investigation of a dendritic methano[60]fullerene octadeca-acid (DA) and its tert-butyl ester (DE) are reported. DE possesses photophysical properties typical of a [60]fullerene mono-adduct with a singlet oxygen quantum yield approaching unity in toluene and a triplet absorption spectrum with a maximum at 710 nm. In methanol DA also possesses properties typical of a [60]fullerene mono-adduct, but in aqueous solution its photophysical behaviour shows a degree of aggregation that is a function of pH and concentration. At pH 7.4 and higher, Coulombic repulsion between de-protonated carboxylate groups reduces the propensity to aggregation and dilute solutions ( $< \sim 10^{-4}$  M) of DA exhibit typical [60]fullerene mono-adduct behaviour, although the singlet oxygen yield of 0.75 is lower than in methanol (0.93). The rate constant for DA triplet state quenching by oxygen in water (pH 7.4) is relatively low, which reflects shielding of the hydrophobic C60 core by the dendrimer thus reducing the possibility of orbital overlap with oxygen due to restricted diffusion. Aggregation is evident from the UV-VIS absorption spectra at concentrations exceeding  $\sim 10^{-4}$  M in water at pH 7.4, beyond which substantial positive deviations from the Beer-Lambert law are observed. In acidic solutions (pH 4.5) the degree of dissociation of the carboxylic acid groups is negligible and the lack of Coulombic repulsion between DA molecules leads to extensive aggregation, even in dilute solutions. In such solutions the singlet oxygen quantum yield is greatly reduced ( $\sim 0.13$  at pH 4.5).

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