Dendrimers with a fullerene core

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On account of their fascinating structures and properties, dendrimers have attracted increasing attention in the past few years. This interest is mainly related to the capability of a dendritic architecture to generate specific properties. For example, a dendritic framework can surround active core molecules, thus creating specific site-isolated microenvironments capable of affecting the properties of the core itself. As part of this research, we have recently shown that dendrimers with a fullerene core are good candidates to demonstrate the shielding effects resulting from the presence of the surrounding dendritic shell.[1-2] In this paper, we now report a new series of dendrimers with a fullerene core. They have been obtained by cyclization of dendritic bis-malonate derivatives at the carbon sphere. The resulting bis-methanofullerene derivatives have been characterised by electrospray (ES) and/or MALDI-TOF mass spectrometries. UV-VIS absorption spectra, fluorescence spectra, and fullerene singlet excited state lifetimes have been determined in solvents of different polarity (toluene, dichloromethane, acetonitrile) and suggest a tighter core/periphery contact upon increase of solvent polarity and dendrimer size. In all the investigated solvents, the fullerene triplet lifetimes are steadily increased with the dendrimer volume, reflecting lower diffusion rates of O_2 inside the dendrimers along the series. Measurements of quantum yields of singlet oxygen sensitization indicates that longer lived triplet states generate lower amounts of singlet oxygen ($^1O_2$*) in dichloromethane but not in apolar toluene suggesting a tighter contact between the dendritic branches and the fullerene core in CH_2Cl_2. In acetonitrile, the trend in singlet oxygen production is peculiar. Effectively, enhanced singlet oxygen production is monitored for the largest dendrimer. This reflects specific interactions of excited $^1O_2$* molecules with the dendritic wedges, as probed by singlet oxygen lifetime measurements, possibly as a consequence of trapping effects.

Acknowledgements

This work was supported by the CNR, the CNRS and the French Ministry of Research.

References

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