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Dendritic Metalloporphyrin-Fullerene Conjugates – Changing the Microenvironment Around Redox-Active Centers and Its Impact On Charge Transfer Reactions

Dirk M. Guldi
Universität Erlangen-Nürnberg

Photophysical investigations on a series of (2,4,6)-tris-substituted metalloporphyrin-fullerene conjugates revealed the effects of an electron rich microenvironment surrounding the electron donating porphyrin as a function of the metal center. On one hand, for all conjugates – water-soluble and non water-soluble – ultrafast charge separation was observed upon photoexcitation. On the other hand, when examining the charge recombination dynamics for the non water-soluble conjugates it becomes obvious that the (2,4,6)-tris-substitution stabilizes the radical ion pair state relative to the mono-substitution in the ortho-, meta-, and para-position. The more efficient protection of the electron donating porphyrin from solvation is thought to be the major cause for this impact. Nevertheless, the situation is slightly different for the water-soluble conjugates. At first glance, the radical ion-pair state lifetimes are also in the case of the (2,4,6)-tris-substitution longer than for the mono-substituted ortho-, meta- and para-conjugates. Upon closer inspection, they fail, however, to exhibit any metal dependence. Competing with the protection from solvation of the dendrons, dipole-charge interactions impact the stabilization in the polar aqueous environment and, in turn, become the dominant force governing the electron transfer dynamics.