Elucidating the Ultrafast Dynamics of Photoinduced Charge Separation in Metalloporphyrin-Fullerene Dyads Across the Electromagnetic Spectrum

Metalloporphyrins are prominent building blocks in the synthetic toolbox of advanced photodriven molecular devices. When the central ion is paramagnetic, the relaxation pathways within the manifold of excited states are highly intricate so that unravelling the intramolecular energy and electron transfer processes is usually a very complex task. This fact is critically hampering the development of applications based on the enhanced coupling offered by the electronic exchange interaction. In this work, the dynamics of charge separation in a copper porphyrin-fullerene are studied with several complementary spectroscopic tools across the electromagnetic spectrum (from near-infrared to X-ray wavelengths), each of them providing specific diagnostics. Correlating the various rates clearly demonstrates that the lifetime of the photoinduced charge-separated state exceeds by about 10-fold that of the isolated photoexcited Cu\textsuperscript{II} porphyrin. As revealed by the spectral modifications in the XANES region, this stabilization is accompanied by a transient change in covalency around the Cu\textsuperscript{II} center, which is induced by an enhanced interaction with the C\textsubscript{60} moiety. This experimental finding is further confirmed by state-of-the-art calculations using DFT and TD-DFT including dispersion effects that explain the electrostatic and structural origins of this interaction, as the Cu\textsuperscript{II}P cation becomes ruffled and approaches closer to the fullerene in the charge-separated state. From a methodological point of view, these results exemplify the potential of multielectron excitation features in transient X-ray spectra as future diagnostics of subfemtosecond electronic dynamics. From a practical point of view, this work is paving the way for elucidating out-of-equilibrium electron transfer events coupled to magnetic interaction processes on their intrinsic time-scales.