Understanding the processes in which the photoinduced electron transfer takes place in dyads is important in designing artificial photosynthetic systems which mimic the natural photosynthesis and also when developing molecular electronic devices from these systems. During the past decade porphyrin-fullerene dyads have gained a lot of attention when studying photoinduced electron transfer. The knowledge of the effects of the orientation and the distance between porphyrin and fullerene on the properties of the electron transfer is essential when designing dyads, which harvest solar energy in an efficient manner and create an electrochemical potential via a charge-separated state.

In this work, ground state properties and electronic excitations of a non-bonded porphine-buckminsterfullerene (H₂P···C₆₀) dyad have been studied in several different orientations of fullerene (i.e. several stereoisomers) with respect to the porphine plane. The density functional theory (DFT) is used to determine the ground state geometries and electronic structures. Electronic excitations and oscillator strengths are obtained from time-dependent density functional theory (TDDFT) calculations. The existence of states related to a photoinduced electron transfer is also studied. Porphine and buckminsterfullerene are selected for computational modelling without chemical linkers, because experimental observations of the complete charge separated state [1] and the formation of an exciplex state [1] for a covalently bonded porphyrin-fullerene dyad raise the question whether these states can also be found by using theoretical methods for similar, but structurally simpler systems.

The orientation of fullerene with respect to the porphine plane is found to affect the equilibrium distance between H₂P and C₆₀. The excitation energies of different stereoisomers are found to differ. The calculations reveal the existence of an excited charge transfer complex state (exciplex state) and a locally excited donor (porphine) state as well as a locally excited acceptor (fullerene) state for all stereoisomers.