Ultrafast Mapping of Solar Energy Conversion

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Singlet Fission (SF) has become a widely discussed phenomenon in recent years due to its potential to circumvent the Shockley-Queisser limit by generation of two charge carriers from two separated triplets formed from an initially excited higher-lying singlet, and thus making better use of the high-energy part of the solar spectrum. The specifics of the mechanism of SF are however still elusive[1]. The struggle to determine this mechanism is largely related to the complex nature of the interplay of electron movement and structural rearrangements of the molecules carrying out SF. We aim to shed light on this interplay by experimentally tracking the structural changes taking place during SF using time-resolved X-ray solution scattering (TR-XSS) for two covalently linked para-bis(ethynyltetracenyl)-benzene (p-BETB) dimers with different side groups, which are expected to show significant structural rearrangement during the SF process by rotating around the central linker[2]. This rotation is thought to be associated specifically with decorrelation of the intermediate triplet pair state, ${}^1(T_1T_1)$, into separate triplets, $(T_1\text{---}T_1)$. As TR-XSS can directly probe structural changes of the dimers and the solvent shell on a sub-picosecond to picosecond timescale as SF takes place, this would give a direct indication of the importance of specific structural changes in the molecule and solvent effects[3]. The mapping of the scattering to underlying changes in the molecule can be achieved by comparison to a theoretically determined model of the scattering signal. Modelling of the scattering signal is however also complicated by the non-trivial description of the involved states, particularly the correlated triplet pair state[1]. The figure below shows already predicted signals for different rotation angles considering an ensemble of structural conformers. We aim to refine this model of the scattering behavior of these dimers so it includes a range of different structural conformers that may exist at each step of the SF process, as well as advanced descriptions of the electronic character, in order to correlate these combined structural and electronic effects with the directly measured structural changes captured by TR-XSS.

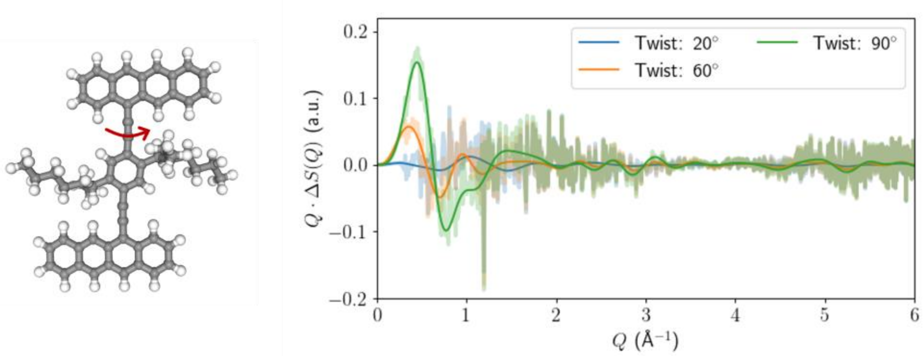

Figure 1: One of the dimers included in the study with the relevant structural change indicated by the red arrow, along with the expected solute scattering signal associated with the structural change (including modelled noise).

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References

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