

Towards Improving Light-activated Functional Molecules

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Photo-induced transformations of molecular systems have high potential for realizing high-density molecular devices applicable in data storage, switches, and light-harvesting, to name a few. In order to design efficient light-activated functional molecules, understanding the fine details of the elementary physical steps in related transformations is essential. Combining the traditional toolset of pump-probe experiments, the novel ultrafast hard X-ray probes, and quantum chemical calculations, one can obtain the necessary information to understand the light-induced ultrafast dynamics, and reveal the mechanistic details of the relaxation processes.[1] The experimental data available from XFELs on molecular systems correlates well with theoretical modelling, which encourages us to exploit theoretical methods to design modifications of the functionality *via* introducing changes to the potential energy landscape by substitution or by solvent effects. With this goal in mind, we have studied suitably modified variants of the $[\text{Fe}(\text{terpy})_2]^{2+}$ complex.

A selected approach involved varying the stability of the excited quintet state by way of modifying the ligands of the homoleptic complexes through chemical substitution. DFT calculations suggested that the energy barrier between the quintet and singlet states can be altered significantly upon substitution, inducing the quintet lifetime to vary by an order of magnitude. The corresponding ligands and complexes were synthesized accordingly, the substituent effect on the lifetime was determined experimentally, and good agreement was found with the trend expected from the DFT-calculated energy barriers. X-ray scattering further supports the energetics obtained from DFT. The agreement between theory and experiment demonstrates that once we have obtained a reliable description of the relevant potential energy surfaces of a given molecular system, we can use quantum chemical computations to rationally tailor these properties by introducing suitable modifications. This should pave the way to advancing ligand engineering of functional molecules to a wide range of applications. The potentials for the ESRF ID09 beamline to take part in this adventure will also be discussed.

References

[1] G. Vankó *et al.*, J. Phys. Chem. C **119**, 5888 (2015); M. Pápai *et al.*, J. Phys. Chem. Lett. **7**, 2009 (2016).