Temperature dependent properties of conjugated polymers – molecular insight from quantum chemistry

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Computational chemistry has long served as an explanatory tool for experimentally obtained results of polymers intended for use in organic photovoltaics (OPVs). Calculated properties on the molecular level permits qualitative explanation of experimentally observed phenomena, promoting understanding of the Structure–Property relationship. Quantitative predictions of polymer properties are also possible, although challenging due to differences in conditions between experiment and calculation, with respect to e.g. temperature.

The temperature dependent optical properties of a series of polymers have been investigated experimentally and computationally. With increasing temperature, the absorption is weakened, broadened, and blue-shifted. This is explained in terms of entropically driven population of more twisted conformations, weakening the conjugation. A computational strategy based on Boltzmann statistically sampled conformations, is used to accurately reproduce the experimentally found trends.

Charge mobility as a function of temperature has been studied experimentally in the well-known donor–acceptor polymer TQ1. With a molecular orbital argument, we show that the experimental results can be explained by thermally induced conformational variations.

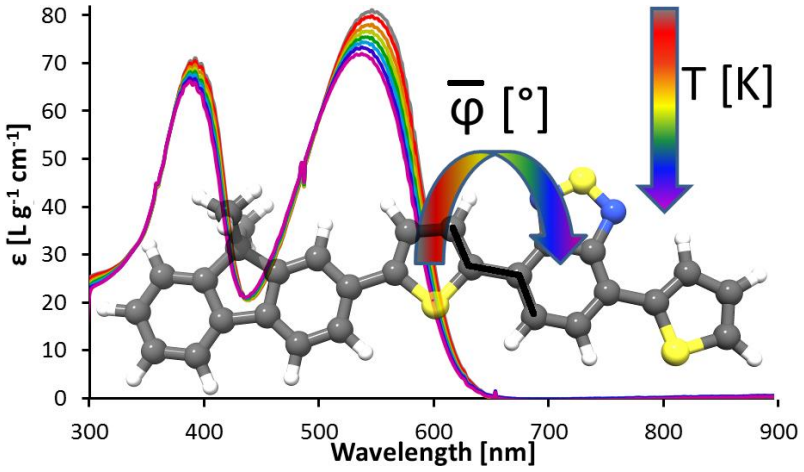

Figure 1. At higher temperatures T, the polymers have on average larger dihedral angles φ, leading to weaker and blue-shifted absorption.

References

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