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Gas-Phase Excited State Dynamics of Bithiophenes

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Introduction

Polythiophenes are ubiquitous in organic photovoltaics (OPVs), playing both the role of chromophore, electron donor and conducting polymer. The ability to generate charge separated states for electrical power depends on the broadness and intensity of electronic transition, and the efficiency with which long-lived states are formed. But does the ability to form long-lived, exploitable states come from the individual monomers or an interplay between several monomers?

For this reason, the structural motif in polythiophenes responsible for generating exploitable, long-lived states is investigated here.

Abstract

The excited state dynamics of polythiophene models were investigated using gas phase Time-resolved Photoelectron Spectroscopy. The results show that the efficient formation of long-lived states is not due to monomer structure. The smallest effective model system was a bithiophene, which showed signs of triplet state formation within femtoseconds. The resulting states were found to live to longer than 400 ps in the gas phase, and shows very different behavior from that in solvent. These results will help unravel which properties of the polythiophenes are intrinsic molecular properties, and which are solvent-molecule interactions.

Experimental Setup

Using Velocity Map Imaging (VMI) we recorded the gas-phase Time-Resolved Photoelectron Spectra (TRPES) of the three compounds thiophene (TP), 2,5-dimethylthiophene (DTP) and 2,2’ bithiophene (BTP), see the main figure. The pump-probe delays were scanned from 0 to 4 ps for TP and DTP and from 0 to 400 ps for BTP. For TP and DTP a 201 nm pump photon with 280 nm probe photon was used, while for BTP a 289 nm probe photon with 400 nm probe through a [1+2] ionization was used.

Discussion

The very short-lived singlets formed in TP and DTP are probably due to conical interactions along the C-S bond breaking coordinate. (Weinkauf et al.) In BTP the excited molecule is not taken to the C-S bond-breaking region but instead into the ring torsion coordinate, were efficient coupling to the triplet state removes population from the S₁ state (Kölle et al.). The BTP TRPES data shows three transients with different decay times. These can be explained by an initial efficient crossing into the triplet states found close to the Franck-Condon region followed by a slower crossing after relaxation, and finally a decay of T₁, which lives longer than 400 ps.

Conclusion

The excited state dynamics of polythiophene is derived from neither the monomeric structure nor the substitution pattern, but from the coupling between two or more monomers. This coupling has previously been shown to occur along the ring-torsion coordinate. We hypothesize that once in the triplet state BTP is dependent on energy from the environment to reach a conical intersection to revert to the ground state. Further work on this system will include restriction of the ring-torsion coordinate to see whether the efficient crossing is prevented.

References


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