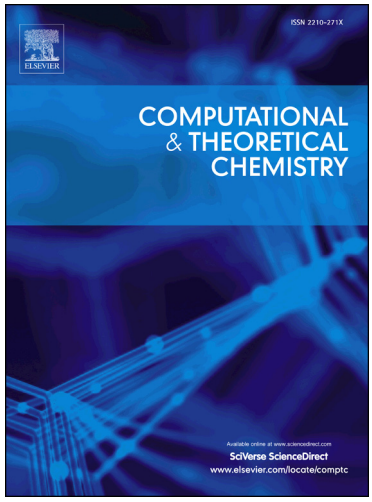

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Quantum dynamics of ultrafast exciton relaxation on a minimal lattice

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Abstract

A combined electronic structure and quantum dynamical study is presented that addresses the nature of the low-lying excitonic states in thiophene oligomers, and the evolution of such states in the presence of a torsional defect. Electronic structure calculations for a thiophene hexamer are carried out using the Second-Order Approximate Coupled-Cluster (CC2) method in conjunction with a transition density analysis. The latter analysis connects to an electron-hole quasi-particle representation that is subsequently used in the quantum dynamical description. Quantum dynamical propagation using the Multi-Configuration Time-Dependent Hartree (MCTDH) method is carried out on a minimal six-site lattice, yielding a basis of 36 electron-hole states in accordance with a Merrifield exciton model. The analysis accounts for vibronic coupling to site-correlated inter-ring stretch modes and a central ring torsional mode that in turn interacts with a dissipative harmonic-oscillator bath, similarly to our recent study of oligo-(*p*-phenylene vinylene) systems [Binder, Wahl, Römer, Burghardt, Faraday Discuss., **163**, 205 (2013)]. The dynamical description illustrates how a partially delocalized initial exciton coherently expands across a torsional defect and converges to a local exciton ground state on a larger fragment within about 300 femtoseconds. Exciton relaxation is found to occur as an intrinsic property of the finite-dimensional lattice structure featuring vibronic couplings.

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