

Photoinduced Electron Transfer in an Ethyne Bridged Donor-Acceptor Complex Depends Strongly on Torsion Angle

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Abstract: Photoinduced electron transfer (ET) between electron donor (dimethylaniline) and acceptor (N-isopropyl-1,8-naphthalimide) covalently linked by ethyne bridge is investigated by a mid-IR transient absorption spectroscopy and TD-DFT computations. We found that electronic and vibrational properties of the complex, including ET rate, depends strongly on the D-A torsion angle.

ET process is essential for a wide range of natural and technological processes, including photosynthesis and energy storage. Electron transfer rate in compounds with covalently linked donor, bridge, and acceptor (DBA) depends critically on the type and length of the bridge. Conjugated bridges offer strong D-A coupling supporting faster ET rates. Alkyne bridges attracted increased attention due to their rigidity and linear structure. While rigid, alkyne bridges themselves do not prohibit torsional motion – the longer the bridge, the smaller is the rotational barrier. At the same time, the extent of conjugation across the bridge is dependent on the torsion angle, so is the ET dynamics. Here we report on ET dynamics in DBA with dimethylaniline donor and N-isopropyl-1,8-naphthalimide acceptor linked with an ethyne bridge. The ethyne bridge is short and limits the freedom to attain all rotational conformations. Transient absorption (TA) measurements in the visible and mid-IR regions were performed to understand the torsion angle dependent ET dynamics. TA experiments in the visible region provided details of the electronic excited state dynamics. The mid-IR TA measurements were focused on carbonyl stretching modes of the acceptor and C≡C stretching mode of the bridge, providing detailed accounts of the changes in electronic states of the complex. Analyzing the spectral changes in the TA experiments and comparing them with TD-DFT-computed spectra for different electronic states resulted in understanding of the overall conformation-dependent ET process. Several characteristic times were observed in the TA measurements. The combined experimental and computational approach resulted in attributing the fastest time component (0.6 ps) to vibrational cooling, the second time component of 3-4 ps to faster electron transfer through $S_2 \rightarrow S_1$ relaxation, the third time component of 38-51 ps to torsional conformation changes and the slowest time component of 1.4 ns to the slow relaxation of the charge separated state (S_1) to the ground state. A large variation of the excited state energies of S_1 (CSS) and S_2 , their coupling strength and oscillator strengths, as well as the frequency and oscillator strength for the C≡C vibrational mode with torsion angle was found from TD-DFT calculations and TA data. These findings suggest that the ET dynamics can be controlled by changing the dihedral angle. The steeper energy barrier ($3k_B T$) to achieve 90° conformation indicates the limited freedom to attain all rotational conformations which is helpful to tune the ET dynamics in a more controllable fashion. The studied DBA complex is a promising system for interrogating ET modulation by exciting the C≡C stretching mode of the bridge. The work is supported by the National Science Foundation (CHE-1954853).