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Ultrafast Structural Dynamics in Various π -Conjugated Molecular Systems Probed by Time-resolved Electronic and Vibrational Spectroscopy

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Abstract

Aromaticity, the special energetic stability derived from cyclic $[4n+2]\pi$ -conjugation, has been the topic of intense interest in chemistry. Recently, the pioneering work by Colin Baird on aromaticity reversal, postulating that aromatic (antiaromatic) character in the ground state reverses to antiaromatic (aromatic) character in the lowest excited triplet state, has attracted much attention. The completely reversed aromaticity in the excited states provides direct insight into understanding the properties of photoactive materials. However, most studies on excited state aromaticity have been based on the theoretical point of view. Time-resolved optical spectroscopies can provide a new and alternative avenue to experimentally evaluate excited state aromaticity. With monitoring ultrafast changes in the excited states, they can provide valuable information for excited state aromaticity. In this regard, recent breakthroughs in experimentally assessing aromaticity reversal in the excited states with time-resolved optical spectroscopic measurements are introduced. Time-resolved electronic and vibrational absorption spectroscopies capture the change of electronic structure and molecular conformations driven by the change of aromaticity and provide clear evidence for aromaticity reversal in the excited states. These approaches will pave a way for the development of new experimental indices for the evaluation of excited state aromaticity and its applications.

Here, we will also discuss the ultrafast coherent exciton dynamics in a series of cofacially stacked perylene bisimides (PBIs). First, we present coherent exciton transport and excimer formation dynamics from the Frenkel state of PBI dimeric and oligomeric H-aggregates. From the vibronic peak ratio analysis in the early-time transient fluorescence spectra obtained by femtosecond broadband fluorescence upconversion spectroscopy, the initial spatial coherence and its evolution are directly unraveled. Second, we introduce symmetry breaking charge separation dynamics via excimer intermediate state in a cyclophane bridged PBI dimer. Based on our observation that the rise time of PBI anion and cation bands in the transient absorption spectra is equivalent to the decay time of the excimer fluorescence, we suggest that the excimer state can effectuate the charge transfer dynamics in the cofacially stacked PBI dimer. Our findings on ultrafast coherent exciton dynamics in various PBI aggregate systems will provide valuable insights into future applications in the field of molecular optoelectronic materials to achieve long-range coherent energy transfer and superb charge transfer efficiency.

Keywords: Femtosecond Broadband Fluorescence Upconversion Spectroscopy, Femtosecond Infrared Spectroscopy, Excited State Aromaticity, Excimer, Symmetry Breaking Charge Separation

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