OA2.6 - Accessing excitonic structure of a photosynthetic Fenna-Matthews-Olson pigment-protein complex by time-resolved circular dichroism spectroscopy

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The steady state circular dichroism (CD) spectroscopy has been providing a wealth of information on the structures of complex molecules. The use of time-resolved circular dichroism (TRCD) spectroscopy was, however, limited to the studies of a few molecules with exceptionally large CD signals due to insufficient sensitivity. We report here the design of a new TRCD spectrometer whose sensitivity is ~100 times higher than that of the previously described setups, which makes that technique suitable to study the dynamics of a wide range of molecular systems in both femtosecond and nanosecond time scales. This setup was applied to measure TRCD spectra of the Fenna-Matthews-Olson (FMO) pigment-protein complex, which is a part of photosynthetic light harvesting machinery of green sulfur bacteria that channels light excitation energy from chlorosomal antenna complex to the reaction center.

A single FMO contains eight strongly coupled BChl molecules leading to excitonic delocalization of the excited states. Due to excitonic nature, the FMO was the first protein complex, for which quantum coherences between the excitonic states were observed in 1997 by the author. The study of coherences in this complex led later to the development of a new technique – two-dimensional spectroscopy. In spite of extensive study of FMO by numerous groups, there is still a debate about the energies of the individual pigments in this system – more than 10 different Hamiltonians have been proposed to model its properties. Unlike conventional absorption, which is sensitive primarily to the spectral positions of the individual pigments and interactions between them, the spectral shape and sign of CD depends strongly on the mutual orientation of the interacting pigments, making TRCD an excellent tool to test the proposed Hamiltonians and refine the excitonic model. In this work we report the first TRCD measurement of the energy transfer dynamics in a photosynthetic complex and compare the experimental results with exciton models based on the proposed Hamiltonians. We also discuss the applicability of TRCD spectroscopy to studies of other photosynthetic systems. (Supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-SC0001341 (S.S.), and as a part of the Photosynthetic Antenna Research Center (PARC), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC 0001035 (R.E.B.)