Two-dimensional electronic spectroscopy using optical pulse shaper: Origin of coherent oscillations in Zn-Naphthalocyanine aggregate

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Two-dimensional electronic spectroscopy (2D-ES) is one of the useful tools to explain molecular structure and dynamics on ultrafast time scale. Mapping the cross-peaks between multilevel energy states in 2D frequency space provides lots of information of quantum mechanical processes such as electronic coherence and excitation energy transfer in molecular aggregate [1-2]. Because of the surprisingly long-lived coherence observed in the 2D-ES which would be a close link to the high efficiency of energy transfer in natural photosynthesis, electronic coherence in photosynthetic system has received much attention over the past few years. However the origin of such a long-lived oscillation is still controversial because vibrational coherence can also show similar oscillating signature in the 2D-ES so that it is hard to distinguish between them [3-4]. To further investigate this issue, we carried out 2D-ES experiment for a mixture of Zn-naphthalocyanine (ZnNPc) molecular aggregate and its monomer. In our experiment, we implement pump-probe geometry using an optical pulse shaper (Dazzler, FASTLITE) to the 2D-ES. A 35fs laser pulse centered at 745 nm is used to measure time-resolved 2D spectra of ZnNPc. The pump and probe beams are injected into the sample cell with 200μm path length. The probe spectrum after the sample is measured by a spectrometer equipped with a CCD detector (100B, PIXIS).

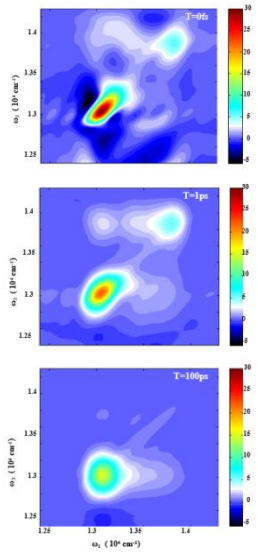

Figure 1. Time-resolved 2D spectra of ZnNPc dissolved in THF at T=0fs, 1ps, and 100ps

Figure 1 shows the 2D spectra of the ZnNPc at population time 0fs, 1ps, and 100ps. At T=0, the 2D spectrum is diagonally elongated due to inhomogeneous broadening. In both diagonal and cross peaks, oscillating signals (700 cm^{-1}) probably associated with the vibrational coherence are observed along T. In particular, one of the cross peaks clearly exhibits a slow beating, indicating the existence of two slightly different oscillation components. The Fourier transform analysis of S(ω1,T,ω3) along T shows the difference frequency between them about 80cm^{-1}, which is in excellent agreement with the result of the Raman spectrum in the ground state. In conclusion, we successfully measured the time-resolved 2D electronic spectra of ZnNPc using the optical pulse shaper. As a future study, we are

planning to extend this 2D approach to 2D chiroptical spectroscopy in combination with the heterodyne-detected chiroptical method [5-6].

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