Supporting Information for

Quantum Beats and Phase Shifts in 2D Electronic Spectra of Zinc Naphthalocyanine Monomer and Aggregate

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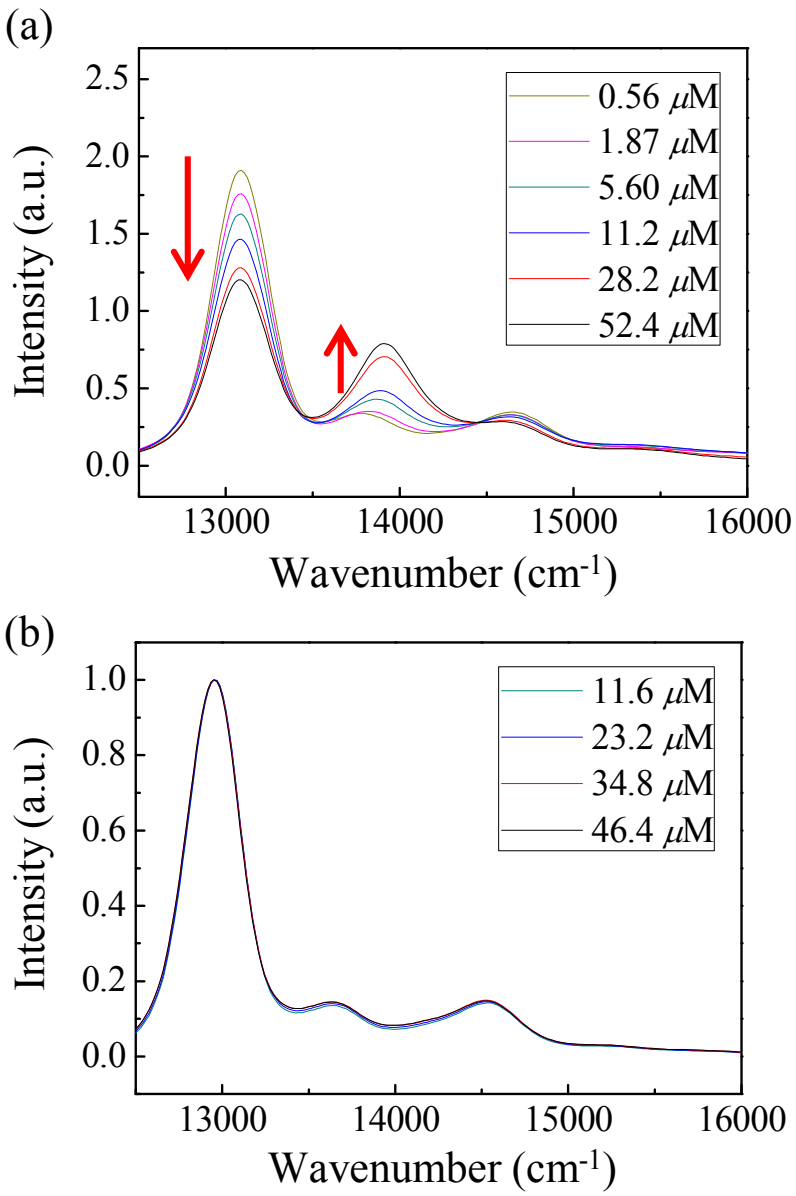

Figure S1. The normalized absorption spectra of the ZnNc in (a) THF and (b) benzonitrile by the total concentration. The absorption spectra in (a) show strong concentration dependence while those in (b) do not significantly change with the concentration, indicating that each aggregate and monomer of the ZnNc form in THF and benzonitrile, respectively.

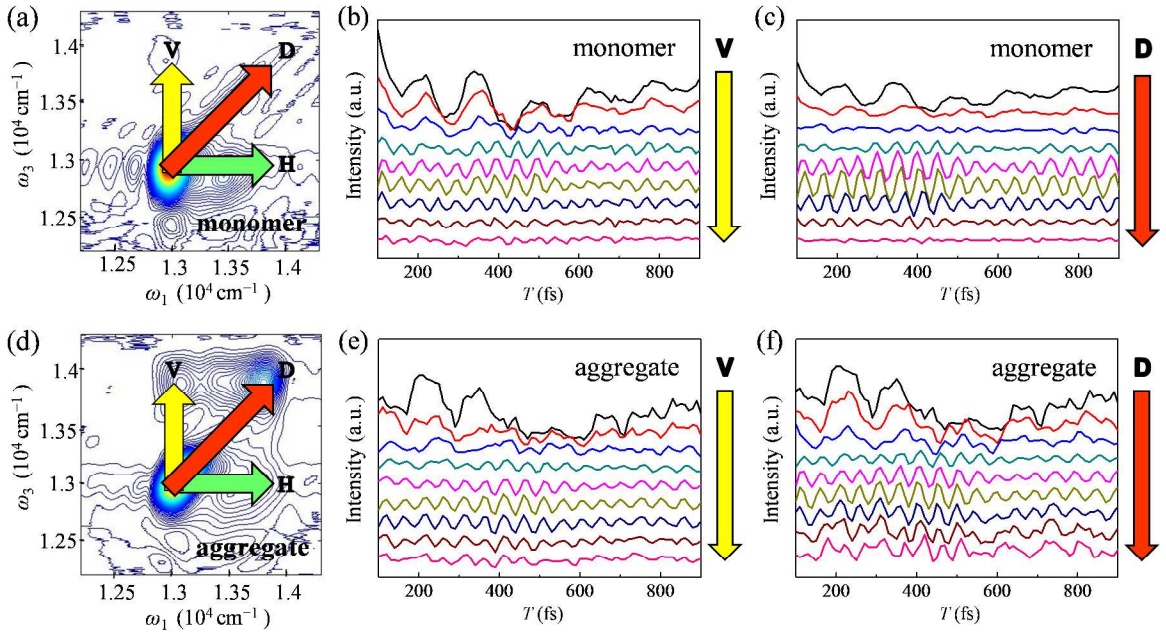

Figure S2. The H (horizontal), V (vertical) and D (diagonal) regions in the 2D spectra of the (a) monomer and (d) aggregate. The temporal oscillations of the V (yellow) and D (red) regions in the 2D spectra of the (b, c) monomer and (e, f) aggregate as a function of T (waiting time). V region (b, e): from ω_3 = 13112cm^{-1} (top) to ω_3 = 13912cm^{-1} (bottom) with 100 cm^{-1} spacing at a fixed ω_1 = 13112cm^{-1}. D region (c, f): from $\omega_1 = \omega_3 =$ 13112cm^{-1} (top) to $\omega_1 = \omega_3 =$ 13912cm^{-1} (bottom) with 100 cm^{-1} spacing.

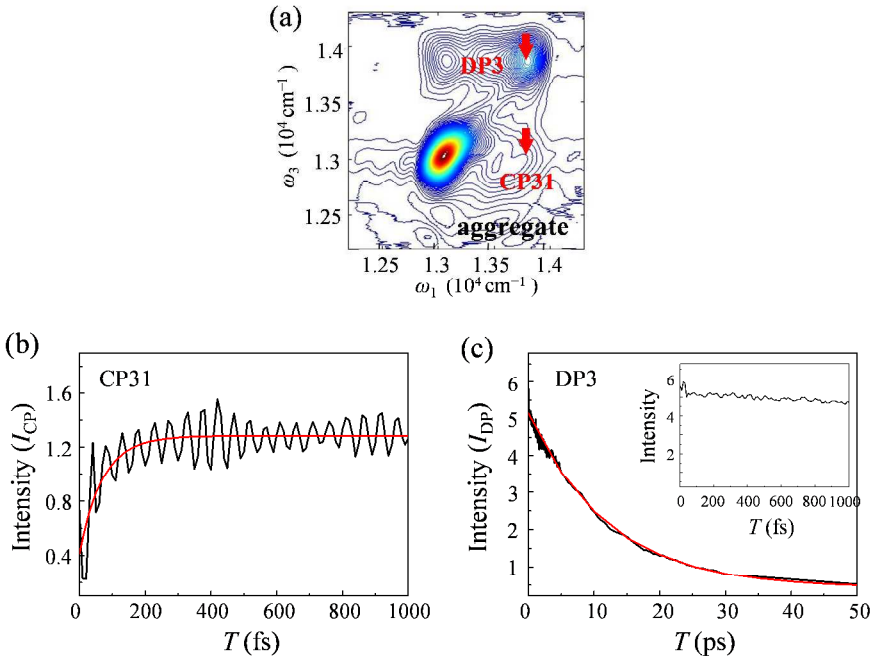

Figure S3. (a) The 2D spectrum of the aggregate at T = 90 fs. The time profiles (I_{CP}, I_{DP}) of the (b) cross (CP31: ω_1 = 13850 cm^{-1}, ω_3 = 13020 cm^{-1}) and (c) diagonal (DP3: ω_1 = 13850 cm^{-1}, ω_3 = 13850 cm^{-1}) peaks in (a) as a function of T. Note that no ultrafast decay component (< 100 fs) is shown in early times of I_{DP} (Inset in (c)). Black: raw data, Red: fitting curves (see Table S1).

Table S1. The fitted time constants (τ) of the time profiles of the CP31 (I_{CP}) and DP3 (I_{DP}) peaks in Figure S3b and S3c. A single exponential rise ($I_{CP}(T) = a_1\{1-\exp[-T/\tau]\}+b_1$) for CP31 and a decay ($I_{DP}(T) = a_2\exp[-T/\tau]+b_2$) for DP3 were used respectively as fitting functions, where $a_{1,2}$ are the positive amplitudes and $b_{1,2}$ the offsets.

Peak position	Time constant (τ)
CP31	70 fs (rise)
DP3	12 ps (decay)

Experimental Setup

The details of the experimental setup for the 2D ES measurement are shown in Figure S4. A 30fs laser pulse centred at 745 nm (13420 cm^{-1}) is generated from a noncollinear optical parametric amplifier (NOPA, ORPHEUS-N, Light Conversion) pumped by a Yb:KGW-doped amplifier system (PHAROS, Light conversion). This is split into two beams, which are used as a pump and a probe, respectively. The pump beam is sent into an acousto-optic pulse-shaper (Dazzler, Fastlite) enabling programmable controls of the complicated parameters of an optical pulse such as the time delay, phase, amplitude, and so on. The Dazzler can produce a duplicated pulse pair and control the variable time delay (t_1) between those replica pulses. For pulse compression, the following steps are taken. First, a prism pair inside the NOPA is adjusted to minimize the pulse width of the probe beam at the sample. The probe pulse width of ~30 fs was measured by using a home-built autocorrelator. Next, a further pule compression of the pump beam is made by the Dazzler to compensate the residual dispersion before duplication of the pump pulse. From the cross-correlation of the pump and probe pulses, it was found that our 2D ES setup has a time resolution of ~40fs. Then, the pump pulse is duplicated using the same Dazzler parameters making the single pump pulse most compressed. The pump (10nJ) and probe (1nJ) pulses are focused into the sample by a CaF_2 convex lens with a focal length of 10 cm. The sample is circulated in a flow cell of 200 μm path length by a micro-flowing pump and the optical density was set to about 0.3 at the peak maximum. The transmitted probe signal is measured by a spectrometer (SP 2300i, PIXIS) equipped with a CCD (100B, PIXIS) as t_1 is scanned.

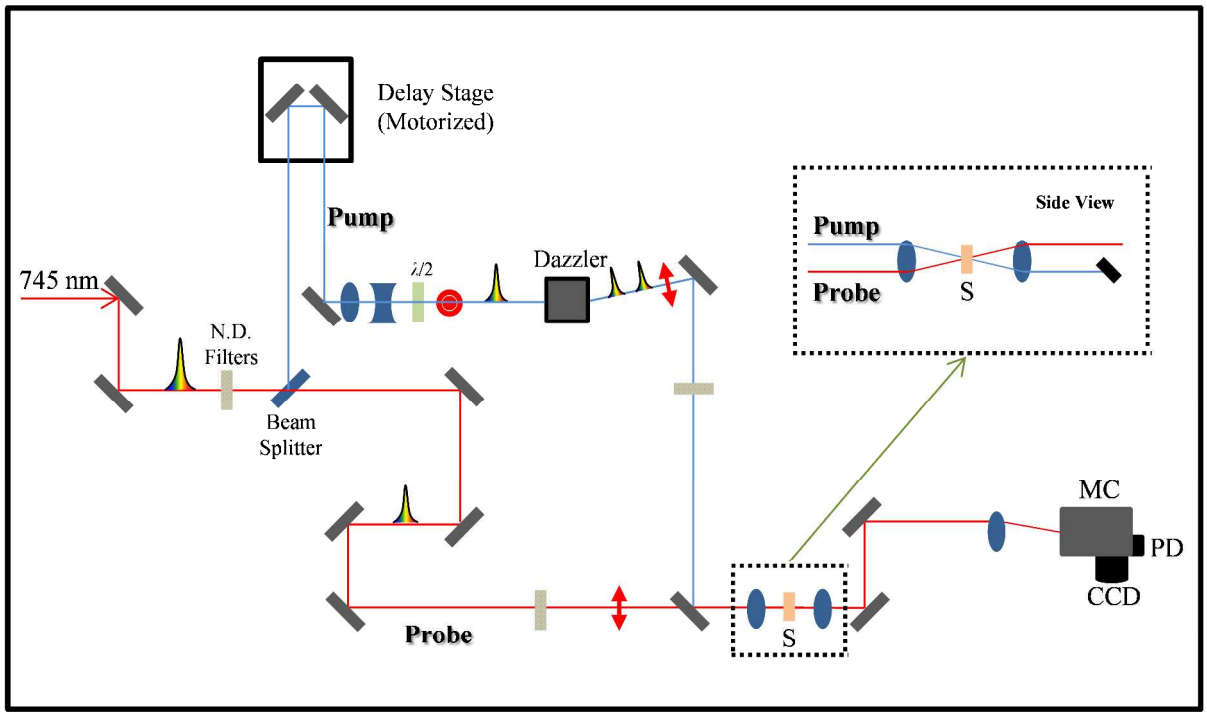

Figure S4. Experimental layout of the 2D ES measurement using the optical pulse shaper (Dazzler). N.D. Filters; neutral density filters, S; sample, MC; monochromator, PD; photodiode, CCD; charge-coupled device detector, λ/2; half-wave plate.