

Supporting Information for

**Photophysics of *meso*- β Doubly Linked Ni(II) Porphyrin
Arrays: Large Two-photon Absorption Cross Section
and Fast Energy Relaxation Dynamics**

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This PDF file includes:

Experimental details on femtosecond Z-scan and TA measurements, electronic natures of absorption bands, Z-scan curves, temporal profiles of femtosecond TA, schematic energy relaxation diagrams, and references.

(1) Experimental details

Femtosecond Open-aperture Z-scan Measurement The two-photon absorption (TPA) cross section ($\sigma^{(2)}$) values were recorded by using the open-aperture Z-scan method¹ with ~130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at 5 kHz repetition rate generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane X). The laser beam was divided into two parts. One was monitored by a Ge/PIN photodiode (New Focus) as intensity reference and the other was used for transmittance measurement. After passing through a plano-convex lens with a focal length of 10 cm, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell was 1 mm. The transmitted laser beam from the sample cell was then detected by the same photo-diode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0 ranged 40 to 60 GW·cm⁻². Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by least-square curve fitting to the observed open-aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)}, \quad (1)$$

where, α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam

After obtaining the nonlinear absorption coefficient β , the TPA cross section $\sigma^{(2)}$ of single solute molecule (in units of 1 GM = 10⁻⁵⁰ cm⁴·s/photon·molecule) can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_A d \times 10^{-3}}{h\nu}, \quad (2)$$

where N_A is the Avogadro constant, d is the concentration of the TPA compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam.

We obtained the TPA cross section $\sigma^{(2)}$ values of hexaphyrins at 1200 nm, where linear absorption is negligible, to satisfy the condition of $\alpha_0 l \ll 1$ in retrieving the pure TPA $\sigma^{(2)}$ values in the simulation procedure. We also measured the TPA cross section value of AF-50 as a reference compound which exhibits 50 GM at 800 nm.

Femtosecond transient absorption measurements Dual-beam femtosecond time-resolved transient absorption (TA) spectrometer consisted of two independently tunable home-made noncollinear optical parametric amplifiers (NOPA) pumped by a Ti:sapphire regenerative

amplifier system (Spectra-Physics, Hurricane X) operating at 5 kHz repetition rate and an optical detection system. The NOPA systems were based on non-collinearly phase-matching geometry and easily color-tuned by controlling a delay between white light continuum seed and second harmonic pump (400 nm) pulses. The generated visible NOPA pulses had a pulse width of ~35 fs and an average power of 10 mW at 5 kHz repetition rate in the range 500-700 nm. The probe beam was split into two parts. One part of the probe beam was overlapped with the pump beam at the sample to monitor the transient (signal), while the other part of the probe beam was passing through the sample without overlapping the pump beam to compensate the fluctuation of probe beam (reference). The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). To obtain the time-resolved transient absorption difference signal at specific wavelength, the monitoring wavelength was selected by using an interference filter. By chopping the pump pulses at 47 Hz, the modulated probe pulses as well as the reference pulses were detected by two separate photodiodes. The modulated signals of the probe pulses were measured by a gated-integrator (SRS, SR250) and a lock-in amplifier (EG&G, DSP7265) and stored in a personal computer for further signal processing. The polarization angle between pump and probe beam was set at magic angle (54.7°) in order to prevent polarization-dependent signals. A quartz cell with a pathlength of 0.5 mm was used in all TA experiments.

(2) Electronic Properties of Absorption Bands

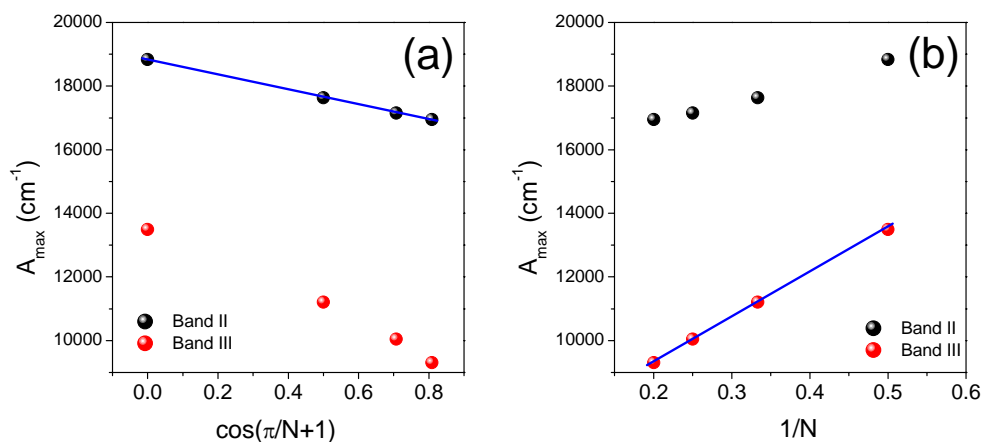


Figure S1. Plot of peak positions of absorption maxima based on (a) excitonic model and (b) particle-in-a-box model.

According to the exciton coupling theory, the relationship of splitting energy between neighboring porphyrin units, ΔE_0 ,

$$\Delta E_0 = \frac{\mu^2}{2\pi\epsilon_0 R^3} \quad (3)$$

where μ is the transition dipole moment and R is the center-to-center distance between chromophores. For example, the exciton splitting energy (ΔE) for low-energy Soret band of larger linear arrays should be given by the following equation,²

$$\Delta E = A_{\max}(\text{band I}) - A_{\max}(\text{band II}) = \Delta E_0 \cos[\pi/(N+1)] \quad (4)$$

where N represents the number of chromophores and A_{\max} is the peak position of absorption maximum for each band. It was assumed that *meso-β* doubly linked Ni(II) porphyrin arrays (**DLNin**) were multichromophoric arrays with a subunit of Ni(II) diphenyl porphyrin. Figure S1(a) shows the character of band II is similar to that of low-energy Soret band in *meso-meso* directly linked porphyrin arrays induced by exciton coupling.³ On the other hand, the character of band III in **DLNin** can be well described by a simple one-dimensional particle-in-a-box model.² In this model, the excitation energy is proportional to the reciprocal value of the number of subunits N in the array. Figure S1(b) shows good correlation with this relationship.

(3) Z-scan Data

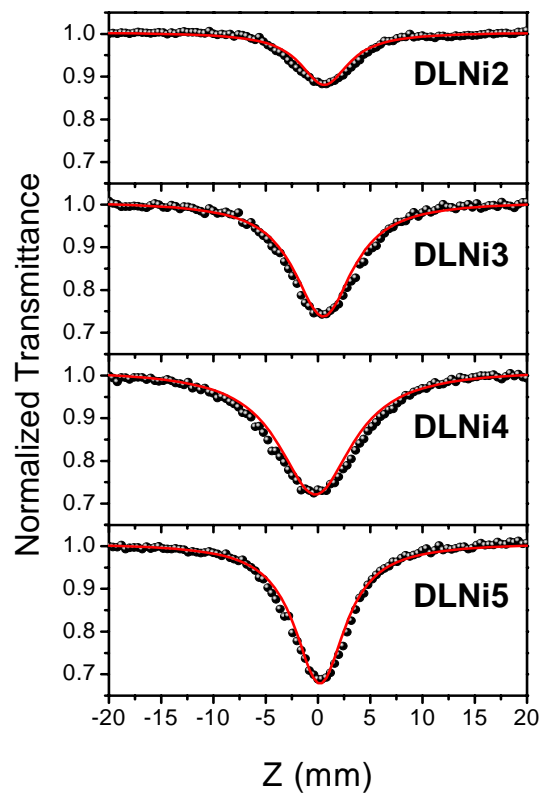


Figure S2. Femtosecond Z-scan data of doubly linked Ni(II) porphyrin arrays in CHCl_3 .

(4) Temporal decay profiles of TA experiment.

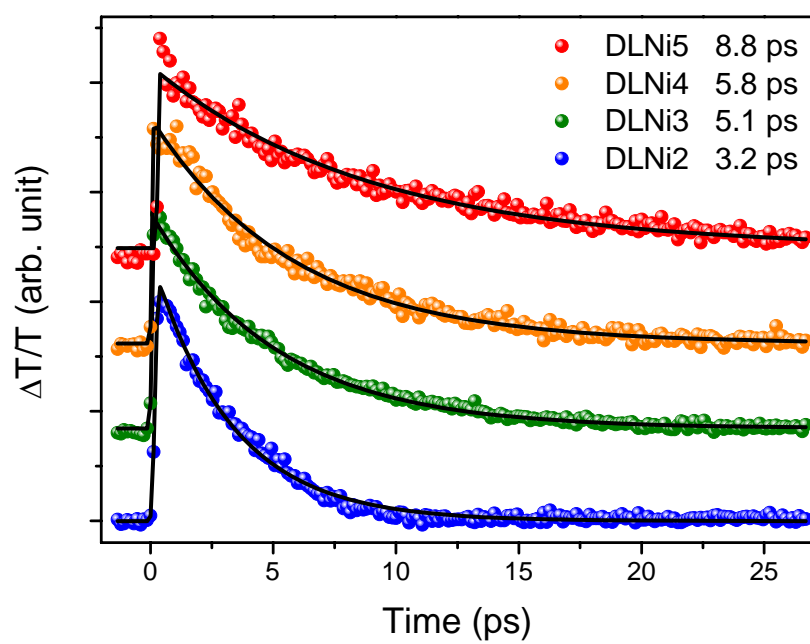


Figure S3. Transient absorption decay profiles for ground-state bleaching recovery signals with photoexcitation of band II region in CHCl_3 .

(5) Schematic Energy Level Diagrams

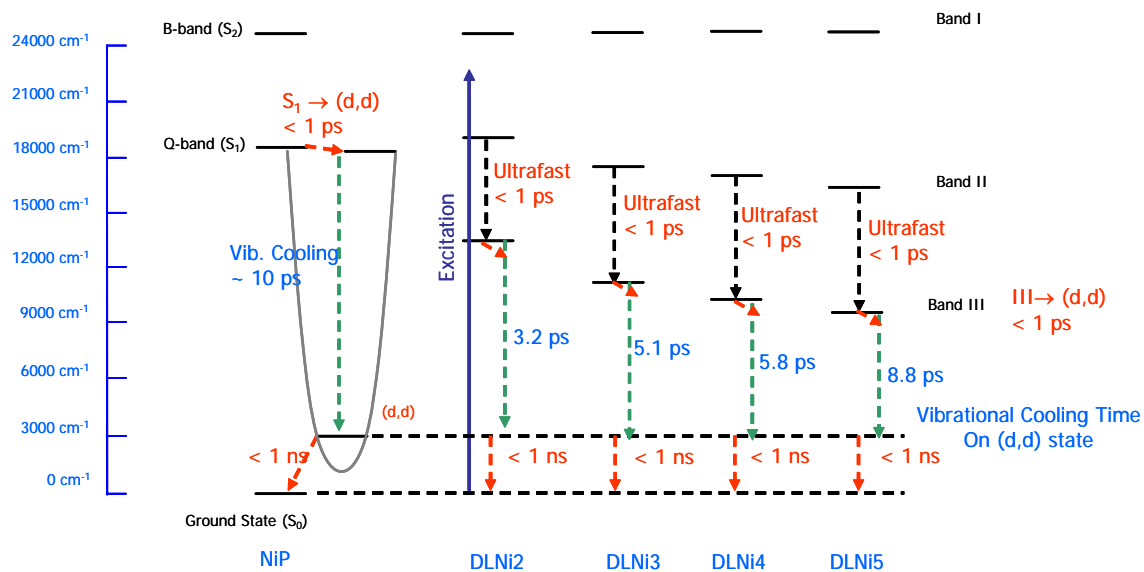


Figure S4. Schematic energy level diagram with ultrafast excitation energy relaxation pathways in doubly linked Ni(II) porphyrin arrays.^{4,5}

Supporting References

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