Supplementary Material (ESI) for Chemical Communications

Supporting Information

Excited-State Energy Relaxation Dynamics of Triply Linked Zn(II) Porphyrin Arrays

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① Experimental details on the femtosecond time-resolved visible and NIR transient absorption spectrometers

② Transient absorption spectra and ground-state bleaching dynamics of **TB2**

Supporting Information

Femtosecond Transient Absorption Spectrum.

The femtosecond time-resolved visible transient absorption (TA) spectrometer was pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate. The generated visible NOPA pulses had a pulse width of ~100 fs and an average power of 1mW in the range 500 - 700 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a 2-mm-thick sapphire window by focusing of small portion of the fundamental 800 nm pulses. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses are monitored by two miniature spectrographs (OceanOptics USB2000+ and OceanOptics NIRQuest). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses excite samples to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-1200 nm region. To minimize chirp, all reflection optics in probe beam path and 2 mm path length of quartz cell were used.

The details of the NIR TA spectrometer used here are described elsewhere.[1] Briefly, two identical home-built optical parametric amplifiers (OPA), pumped by a commercial Ti:sapphire regenerative amplifier (Hurricane, Spectra Physics) with a repetition rate of 1 kHz, are used to generate near IR pulses.[2] Either signal (wavelength < 1600 nm) or idler (wavelength > 1600 nm) pulses of each OPA was selected by a dichroic mirror and served as

a pump or a probe. Energy of pump pulse was kept less than 0.5 μJ and that of probe pulse < 10 nJ. The polarization of the pump pulse was set at the magic angle (54.7) relative to the probe pulse to recover the isotropic absorption spectrum. The broadband transmitted probe pulse was detected with a $N_2(l)$-cooled HgCdTe detector. The pump spot was made sufficiently larger than the probe spot to ensure spatially uniform photoexcitation across the spatial dimensions of the probe pulse. The instrument response function was typically 140 fs.

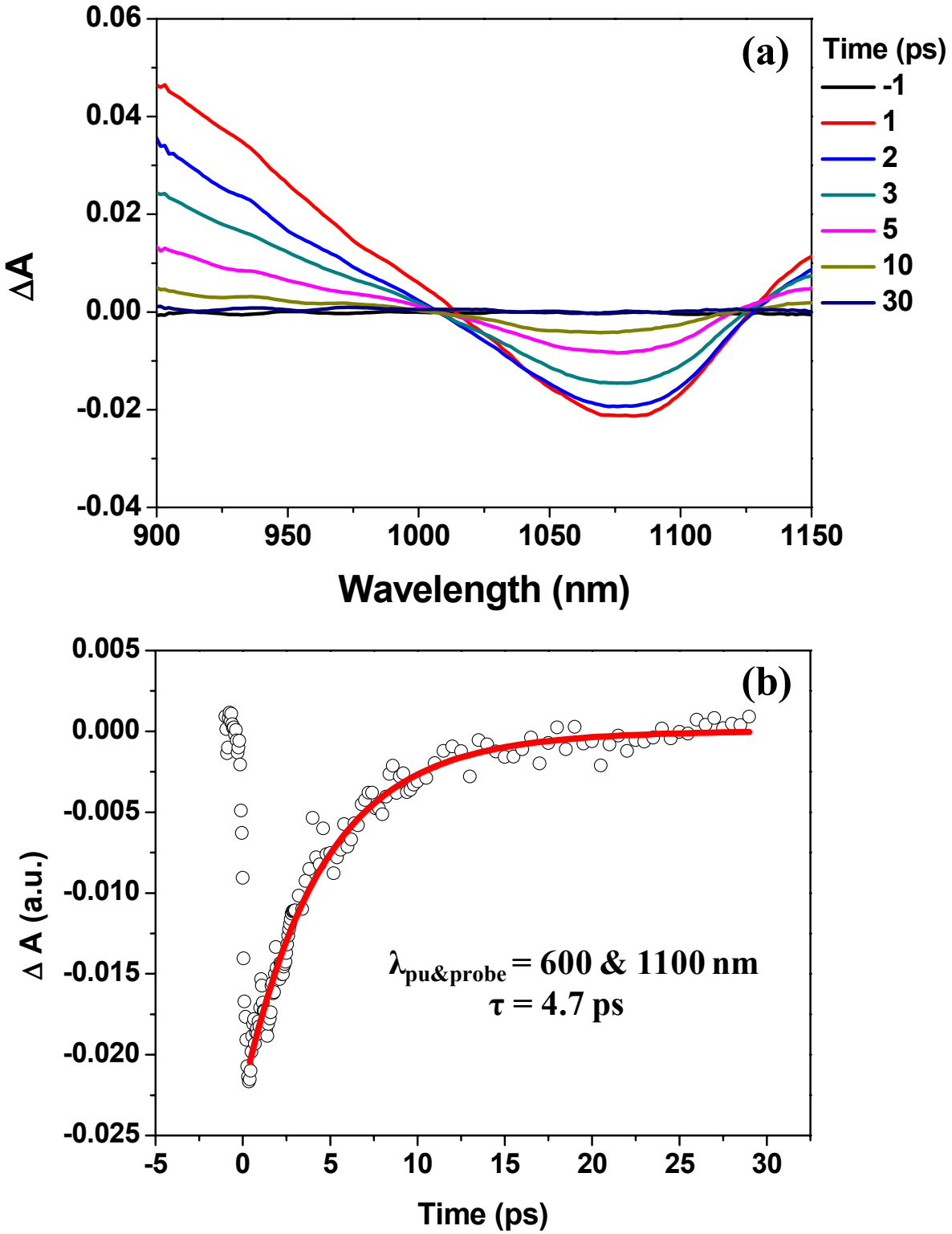

Figure S1. (a) Transient absorption spectra of **TB2** and (b) ground-state bleaching recovery dynamics probed at 1100 nm after photoexcitation at 600 nm.

References

(1) Kim, S.; Jin, G.; Lim, M. *J. Phys. Chem. B* **2004**, *108*, 20366.

(2) (a) Lim, M.; Wolford, M. F.; Hamm, P.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1998**, *290*, 355. (b) Hamm, P.; Kaindl, R. A.; Stenger, J. *Opt. Lett.* **2000**, *25*, 1798. (c) Hamm, P.; Lim, M.; Hochstrasser, R. M. *J. Phys. Chem. B* **1998**, *102*, 6123.