

Supporting Information

Ultrafast Dynamics of Non-Rigid Zinc-Porphyrin

Arrays Mimicking the Photosynthetic “special pair”

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Supporting information

1. *Experimental Methods*

Ultrafast transient absorption (TA) experiments were carried out using UV pump pulses to excite the porphyrin complexes in their Soret band, in order to follow all the relaxation phenomena occurring from these high energy levels. TA dynamics and spectra were acquired by using as a probe the white light generated by a CaF_2 plate, covering the 420–720 nm wavelength range. Two different excitation pulses were used: 1) a narrowband pulse (corresponding to ~ 100 fs pulse duration), with spectrum peaked at ~ 420 nm in order to pump the red edge of the arrays, generated by an optical parametric amplifier (OPA); 2) a short (sub-25 fs duration) pulse with spectrum spanning the 400–430 nm range, obtained by sum frequency generation between visible and infrared noncollinear OPAs¹. The two excitation spectra, together with the absorption spectra of the three compounds, are reported in Fig. S2. For the 100-fs pump pulses, TA spectra were recorded with a commercial 1 kHz ultrafast spectrometer (Helios, Ultrafast Systems) in a magic angle configuration, while for the sub-25 fs pump pulses TA spectra were measured using a

spectrometer equipped with CCD capable of single-shot detection at 2 kHz (Stresing Entwicklungsburo) in a parallel configuration. Samples were diluted in THF and put in 1mm cuvettes for measurements with the 100-fs pulses and in 200 μ m cuvettes for measurements with the sub-25 fs pulses.

Time-resolved fluorescence measurements were performed on a commercial time-correlated singlet photon counting system (Deltaflex, HORIBA Scientific). We used a 406 nm laser diode (DeltaDiode) in order to excite at the Soret band for each molecule and detected the emitted light at 600 nm, with relative polarization between the excitation and emission arms set to magic angle. We used the same solvent employed for TA measurements but with the samples diluted by a factor of 10, in order to avoid re-absorption effects. Absorption measurements (not shown) did not evidence any concentration-dependent modification of the spectrum in the range of dilutions used in this work.

The monomer and arrays of porphyrins studied in this work were synthesized at Arizona State University².

2. Supplementary figures

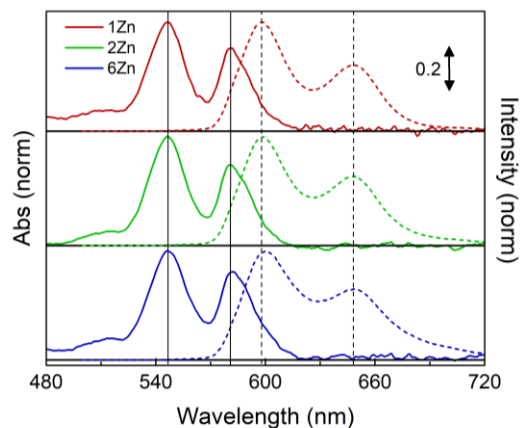


Figure S1: Normalized absorption and emission spectra of the three compounds (1Zn, 2Zn and 6Zn). The absorption is related to the S_1 states (Q bands) and the emission spectra (taken with photoexcitation at 400nm) show the same vibronic replicas for all the compounds. The spectral shift is small in comparison to the change in spectrum observed for the Soret bands

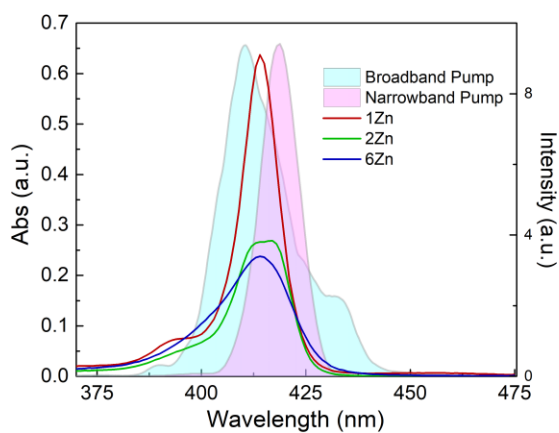


Figure S2: Zoom of the absorption spectra of the Soret (S_2) bands of the compounds and spectra of the pump beams. The narrowband pump (420nm peak, 100-fs duration) was used to measure up to 5ns. The broadband pump (sub-25-fs duration) was used to detect the early time relaxation. The narrowband pump was tuned to the red edge of the S_2 states, avoiding in part the internal relaxation of the excitonic manifold in the arrays.

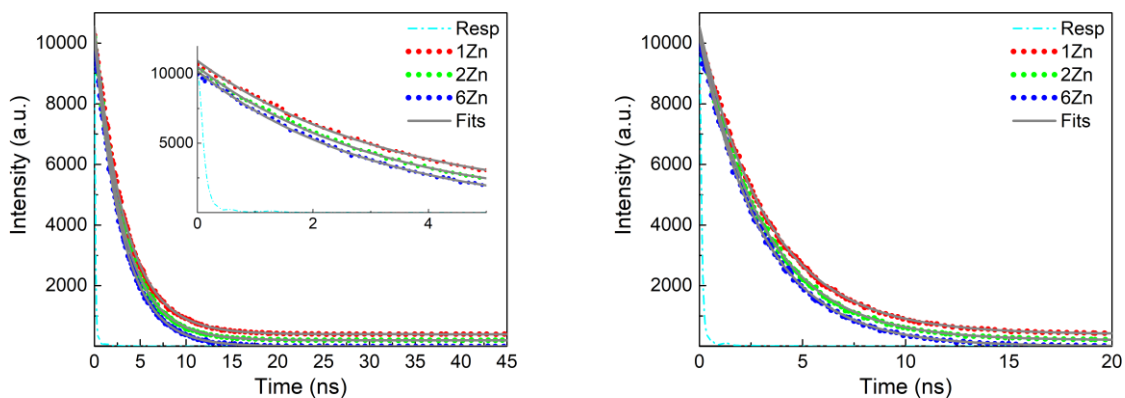


Figure S3: Fluorescence decay traces (points) and mono-exponential fits (solid lines) giving time constants of 3.33ns for 1Zn, 3.13ns for 2Zn and 3.03ns for 6Zn. The fluorescence traces were selected at 600nm.

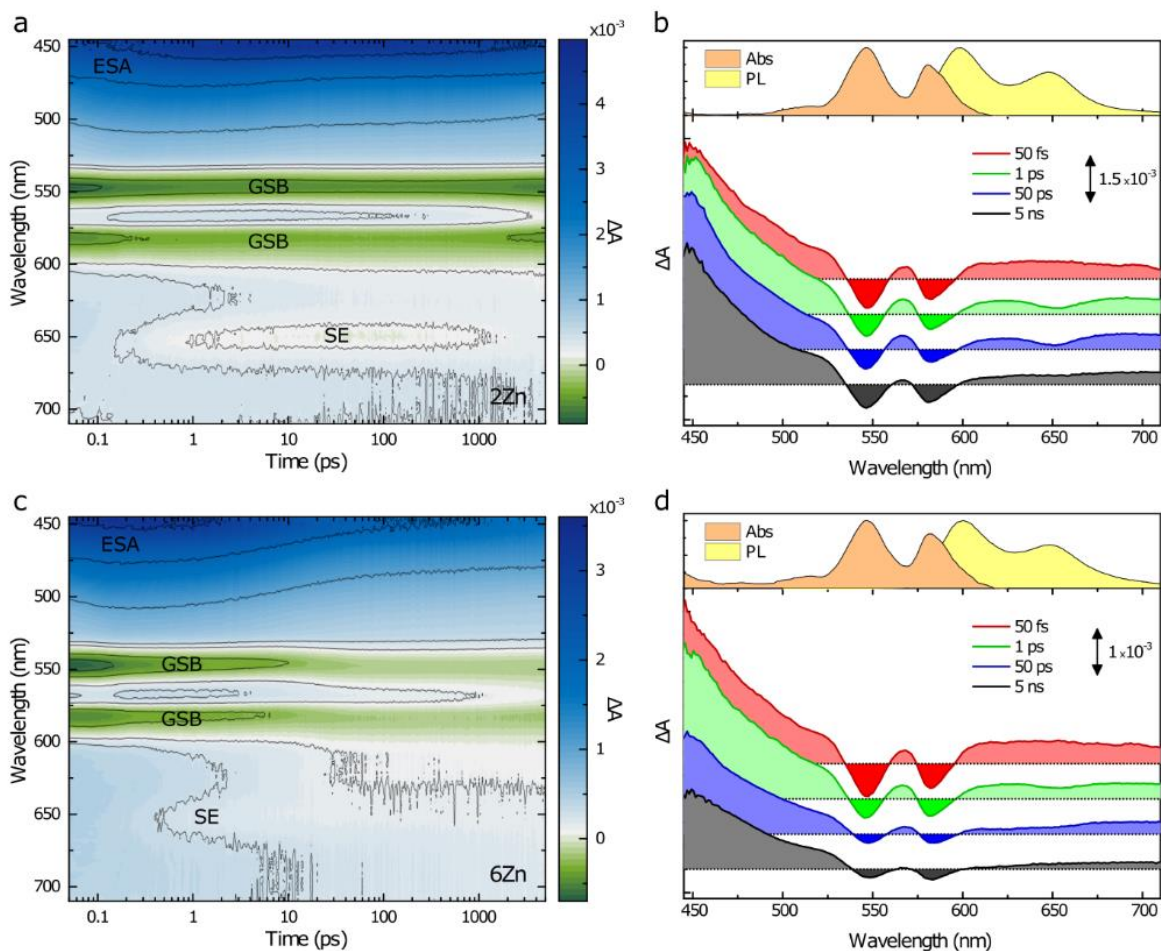


Figure S4: a) ΔA map for 2Zn after excitation with a 420-nm pulse. b) Selected ΔA spectra for 2Zn at different pump-probe delays, together with absorption (orange) and emission (yellow) spectra as references. c) ΔA map for 6Zn after excitation with a 420-nm pulse. d) Selected ΔA spectra for 6Zn at different pump-probe delays, together with absorption (orange) and emission (yellow) spectra as references.

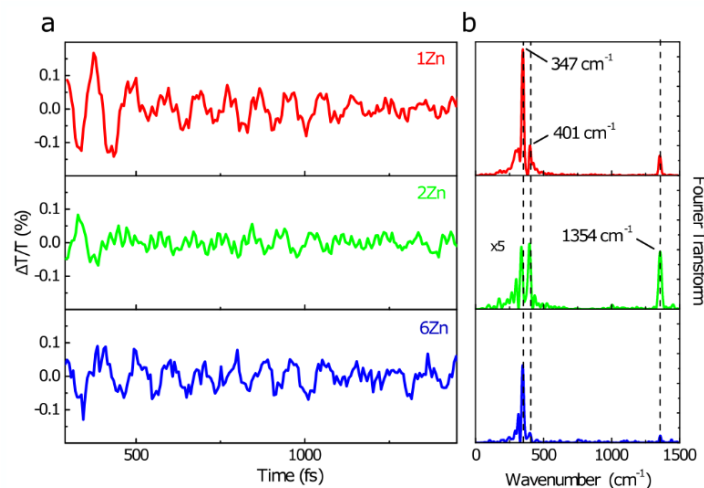


Figure S5: (a) extracted oscillations from dynamics with sub-25-fs pump pulses measured at 425 nm probe wavelength, after subtraction of a bi-exponential decay from the TA dynamics; (b) corresponding Fourier Transforms.

3. S_1 Relaxation Pathways Analysis

In order to evaluate the efficiencies of the decay pathways of the singlet excited state S_1 , we performed an analysis for the monomer case, where we can precisely quantify the branching between the radiative channels and the non-radiative one. From the time resolved fluorescence measurements shown in Figure S3 we extracted the lifetime of the

S_1 state ($\tau_{PL} = 1/k_{PL}$, where k_{PL} is the fluorescence decay rate). This rate represents the

sum of the radiative (k_R) and non-radiative (k_{NR}) rates ($k_{PL} = k_R + k_{NR}$), where in principle k_{NR} describes both ISC and $S_1 \rightarrow S_0$ ground state recovery deactivation channels. By considering the fluorescence quantum yield (ϕ_F) reported by Terazono et al.² defined as $\phi_F = k_R/(k_R + k_{NR}) = k_R/k_{PL}$, it is possible to retrieve the radiative decay time ($\tau_R = 1/k_R$) from the relaxed S_1 state as $\tau_R = \tau_{PL}/\phi_F$. Once calculated the radiative decay time we can retrieve the non-radiative time decay as $\tau_{NR} = 1/k_{NR}$ where $k_{NR} = k_{PL} - k_R$. The experimental and calculated values are reported in Table S1.

	τ_{PL}	ϕ_F	τ_R	τ_{NR}
1Zn	3.33 ns*	0.06	55 ns	3.51 ns

Table S1: Experimental (*) and calculated time decays retrieved for the 1Zn sample for the deactivation of S_1 state. Fluorescence quantum yield calculated in Reference ².

From our TA measurements we note an absence of GSB recovery at nanosecond time scale, suggesting that $S_1 \rightarrow S_0$ deactivation channel is a negligible non-radiative decay pathway and thus we can conclude that τ_{NR} mainly describes the ISC process from S_1 toward the porphyrin triplet state.

We also note that a similar analysis is more challenging for the dimer and the hexamer due to the presence of new ultrafast deactivation channels which affect the population of the emissive S_1 state and consequently the interpretation of the fluorescence lifetime.

REFERENCES

- (1) Manzoni, C.; Polli, D.; Cerullo, G. Two-Color Pump-Probe System Broadly Tunable over the Visible and the near Infrared with Sub-30 Fs Temporal Resolution. *Rev. Sci. Instrum.* **2006**, *77*(2).
- (2) Terazono, Y.; Kodis, G.; Chachisvilis, M.; Cherry, B. R.; Fournier, M.; Moore, A.; Moore, T. A.; Gust, D. Multiporphyrin Arrays with π - π Interchromophore Interactions. *J. Am. Chem. Soc.* **2015**, *137*(1), 245–258.