Electronic Supplementary Information (ESI)

Intrinsic lifetimes of the Soret bands of the free base tetraphenylporphyrin (H₂TPP) and Cu(II)TPP in the condensed phase

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Experimental Section:

Apparatus and procedures

The experimental setup of the fluorescence up-conversion measurement is presented in Fig. S1. The solid-state diode-pumped Nd:YVO4 laser (Verdi V-5, Coherent, 532 nm single-frequency output) was used to pump the cavity dumped Ti:sapphire oscillator (KM Lab.). Bragg cell was used for cavity dumping by acousto-optic modulation from a RF driver (NEOS). We tuned laser pulses so that the output power was around 12 mW at a central wavelength of 800 nm and 15 fs pulse duration at 400 kHz repetition rate. This output beam was compressed to compensate the group delay dispersion (GDD) using a prism pair and focused onto a 200 µm thick BBO crystal by a 50 mm focal length concave mirror to produce frequency doubled pulses. Harmonic separator (HS) is used to separate the pump and probe pulses in Fig. S1. Frequency doubled light (408 nm) was recompressed for compensating the GDD and served as a pump pulse. And the residual pulse is provided as a probe pulse. The residual pulse with 15 fs of the pulse duration was recompressed for compensating GDD. Laser pulses were positively chirped as they passed through optical components. This was compensated by negative chirping through prism pairs. Periscopes were used to control the polarization and height of pulses. The delay time Δt was varied by a precision motorized linear stage (M-ILS200CCHA, Newport) with a travel length of 200 mm and a positional resolution of 100 nm. The sample was kept in a 500 µm thick sample cell (Starna Cells), and the fluorescence is induced by focusing the pump laser pulse with a 100 mm focal length plano-convex lens. The laser polarization axis of the pump pulse was set at the magic angle of 54.7° with respect to that of the probe pulse to avoid the anisotropy effect on the signal due to the sample reorientation. Fluorescence was collected by a reflecting objective (x15, NA0.28, Davin Optronics) lens and overlapped with the probe beam in a 500 µm thick BBO crystal to generate sum-frequency radiation. We tuned the angle of BBO crystal with respect to the propagation direction of the laser pulse by use of a motorized rotational stage to maximize the up-converted signal. The

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up-converted fluorescence signal was focused on the entrance slit of a monochromator (DM150i, Dongwoo optron) and detected by a photomultiplier tube (R3235-01, Hamamatsu). Background signals were eliminated by a broadband pass filter. The photomultiplier tube output was integrated by a photon-counter (SR400, Stanford Research System). The instrumental response function was obtained using cream in water as the scattering source. The cross-correlation band width of 120 fs was obtained at the optical layout for the Soret band measurement, as shown in Fig. S2.



Fig. S1. Schematic drawing of the setup of fluorescence up-conversion measurement.

For transient absorption measurement, frequency doubled beam was split into two equally in front of the delay stage to be used for pump and probe pulses. A chopper was used to measure the change of the signal in the presence or absence of the pump laser pulse. A small portion of the probe beam was separated by a beam-splitter for the reference pulse. The pump and probe beams were overlapped in a sample cell whereas the reference beam was not overlapped with the pump in the sample cell. The autocorrelation width of the pump laser pulse was estimated to be ~ 40 fs by the optical Kerr measurement using carbon disulfide (CS₂), as shown in Fig. S3. Probe and reference pulses were detected by photodiodes. The absorbance (ΔA) was measured by a lock-in amplifier (SR810, Stanford Research System). All data acquisition and all device controls were processed by using the home-made program written with the LabView software. The ambient temperature was 22 ± 1 °C during all measurements.

The equation,

 $S(t) = \sum A_i \exp(-t/\tau_i)$, was used to fit the transient absorption and fluorescence decay signals

including the convolution with a Gaussian instrumental response function.



Fig. S2. The instrumental response function fitted with the Gaussian function with the FWHM of ~ 120 fs at 408 nm of the excitation wavelength.



Fig. S3. The second harmonic pulse used in the transient absorption measurement, showing the FWHM of ~ 40 fs.

Steady-state measurements

Steady-state absorption and emission spectra were recorded on a Jasco V-530 and a Spex Fluorog-3

Luminescence spectrophotometer, respectively.



Fig. S4. The ground-state absorption spectra (a) Soret band and (b) Q-band of $Cu^{II}TPP$ (close circle, blue) and H₂TPP (open circle, red) in benzene. The sample concentration was less than 2 μ M in a 10 mm cell.



Fig. S5. Fluorescence emission spectra of (a) Soret bands and (b) Q-bands of $Cu^{II}TPP$ (close circle, blue) and H₂TPP (open circle, red) in benzene. The sample concentration was less than 10 μ M in a 10 mm cell. The emission spectrum of Cu^{II}TPP at Q-band was magnified 10 times. The excitation wavelength is 408 nm.

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The ground-state absorption spectra of $Cu^{II}TPP$ and H_2TPP in benzene are shown in Fig. S4. The Soret or B-band was located around 420 nm with a single peak. It seems they have a shoulder around 395 nm. The maximum position of absorption spectra of Q-band of $Cu^{II}TPP$ in benzene is 539 nm. Absorption coefficients of the Soret band were estimated to be ~ 20 times larger than those of the Q-band.

Fluorescence spectra of $Cu^{II}TPP$ and H_2TPP in benzene are shown in Fig. S5. All fluorescence spectra at B-band have weak intensity. The feature around 465 nm are ascribed to the Raman signal representing the C-H vibrational mode of the solvent. We detected the fluorescence signal at 450 nm to avoid the Raman signal originated from the solvent.