Intrinsic lifetimes of the Soret bands of the free-base tetraphenylporphine (H$_2$TPP) and Cu(II)TPP in the condensed phase†

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Soret band lifetimes of the free-base tetraphenylporphine (H$_2$TPP) and Cu(II) tetraphenylporphine (Cu^{II}TPP) at 408 nm have been directly measured with femtosecond (fs) resolution using the fluorescence-upconversion technique for the first time, giving τ = 68 ± 15 and 63 ± 15 fs, respectively, in benzene solvent.

Porphyrin molecules have long been spotlighted as model systems not only for the O$_2$ carrier of the cell[1] but also for the investigation of the light-harvesting photosynthetic vehicles in biology.[2] In the latter, the photon is captured by the porphyrin moieties, and the photon energy is then converted to electronic and/or vibrational energy of molecules, eventually driving chemical reactions crucial for the energy consumption and storage in the form of chemical bonds.[3] Thus, porphyrin and its metal derivatives found in biological pigments initiate the first step in the energy cycle of living organisms. The complex structure of the porphyrin molecules leads to their unique photophysical properties of large absorption cross section and ultrashort excited-state lifetimes, which seem to be essential features for efficient photon capturing ability as well as photo-stability. Therefore, the investigation of the photophysical properties of excited states of porphyrin systems is valuable for unravelling the nature of the initial stage of the energy conversion cycle. One of the most studied porphyrin systems is tetraphenylporphyrin (TPP) molecules coordinated with various metal atoms, such as Zn,[4–7] Mg,[6,7] Cd,[6] Co,[8] Ni,[9] VO,[10] Cu.[11] Although the lifetimes and dynamics of the Q bands (S$_1$) in the 500–700 nm region have been relatively well established, the strong Soret bands (S$_2$) at ~400 nm for some TPP molecules show some controversy in terms of the lifetime and relaxation dynamics. For instance, the lifetime of the Soret band of Zn-TPP has been measured by many different research groups, giving the value of 1.6 ± 0.4 ps in nonpolar solvents.[4,5,12] Surprisingly, however, the Soret band lifetime of the free-base TPP (H$_2$TPP) has not been directly measured to date mainly because it is nontrivial to detect such a low fluorescence signal. The Zewail group recently reported the first femtosecond-resolved fluorescence up-conversion transient for the Soret band of H$_2$TPP,[13] but the time resolution was not sufficient for the direct estimation of the corresponding ultrashort lifetime.

Here, we report the fluorescence up-conversion transient with ultrafast time resolution with a cross-correlation width of

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~120 fs, giving the directly-measured fluorescence lifetime of the Soret band of H$_2$TPP for the first time. For the fluorescence up-conversion measurement, a cavity dumped Ti:sapphire oscillator output (~12 mW at the central wavelength of 816 nm; Δt ~15 fs at 400 kHz repetition rate) was split into pump and probe pulses. The pump laser pulse was generated by frequency-doubling using a BBO crystal to give the pulse at ~408 nm and the group delay dispersion was compensated by a prism pair. The delay time between pump and probe pulses, was varied with a time resolution of 0.67 fs. The polarization orientation between pump and probe was set at the magic angle of 54.7° to avoid the anisotropy effect of the reorientation. Fluorescence from the excited sample, collected by a reflecting objective lens, was overlapped with the time-delayed probe pulse to generate sum-frequency radiation in a 500 μm thick BBO crystal. The up-converted signal was then separated in a monochromator and detected by a photo-multiplier tube integrated by a photon-counter. For the transient absorption measurement, both pump and probe laser pulses were at 408 nm, and the cross-correlation width was measured to be ~40 fs. The absorbance as a function of the delay time was measured by a lock-in amplifier.

The Soret band transient shows the asymmetric nature as a function of the delay time between pump and probe laser pulses, clearly showing a lifetime of 68 ± 15 fs for the Soret band of H$_2$TPP at 408 nm in the benzene solvent, Fig. 1. This value is slightly larger than the lifetime estimated by the Zewail group, having the upper limit of 50 fs.[13]

Ultrafast dephasing of the Soret band is reflected as the fast rise of the Q-band fluorescence, Fig. 1. Namely, the appearance rate of the Q-band fluorescence signal matches with the decay rate of the Soret band, indicating that the main dephasing mechanism of the Soret band is the internal conversion to the vibrationally excited level of the Q-state. The origin of the ultrafast decay of the Soret band of H$_2$TPP, however, seems to remain controversial, especially since the corresponding lifetime in the gas phase had been estimated to be ~5 ps,[14] which is two orders of magnitude longer than that in the condensed phase. The intramolecular electronic structure of H$_2$TPP alone cannot explain this large discrepancy. One of the possible scenarios would be that the structural (torsional) change upon the Soret excitation in the gas phase may hamper the internal conversion process occurring at the conical intersection of which the nuclear configuration may be confined at the minimum energy along the torsional coordinate. The photon-induced structural change in the condensed phase, on the other hand, may be hindered due to solvent friction, facilitating the internal conversion process. Namely, in the condensed phase, the structural stress given by the electronic
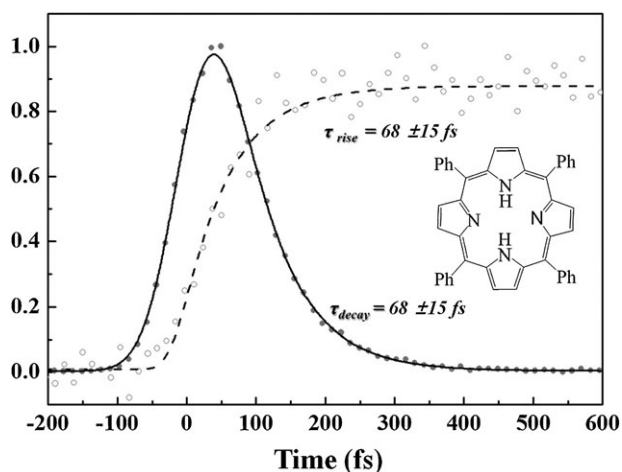
Fig. 1 Time-resolved fluorescence up-conversion transients of the Soret band (●) and Q-band (○) of H_2TPP in benzene at a concentration of 5×10^{-4} M. Solid (Soret band) and dashed (Q-band) lines are fits to the experimental data. The excitation wavelength is 408 nm.

excitation is possibly released rapidly through the fast internal conversion process through the conical intersection. Detailed theoretical calculations and further experiments are certainly desirable for the validation of this or other scenarios.

Another little-studied system is $Cu^{II}TPP$. Fluorescence from the Soret band of $Cu^{II}TPP$ has not been reported in the condensed phase because of the extremely low fluorescence quantum yield. The Soret band lifetime of $Cu^{II}TPP$ is measured to be 63 ± 15 fs from the fluorescence up-conversion transient, Fig. 2. It is interesting to note that Sébastien *et al.* reported the Soret band lifetime of $Cu^{II}TPP$ to be 65 ± 10 fs in the gas phase.[15] They observed biexponential decay though, and it was ascribed to the presence of the charge-transfer state nearby the Soret band. The mere experimental fact that the Soret band lifetime of $Cu^{II}TPP$ is almost same as that of H_2TPP, does not necessarily indicate that their electronic structures and relaxation mechanisms are similar. The difference in the transient absorption spectra of H_2TPP and $Cu^{II}TPP$ using 408 nm as both pump and probe pulses, for example, reflects that the photon-induced structural change in the Soret band is quite different for the two systems, Fig. 3. While both transients show plateaus within the delay time of ~ 6 ps with the instrument-limited fast rise, an interesting femtosecond-resolved modulation is found for the absorption transient for $Cu^{II}TPP$ only. The Fourier-transform into the frequency domain gives rise to the vibrational frequency of 390 cm^{-1}. According to the previous resonance-Raman study[16] this mode corresponds to the metal–pyrrole breathing mode (ν_8), including the Cu–N stretching motion. The experimental fact that this 390 cm^{-1} symmetric A_{1g} mode is strongly modulated in the transient absorption spectrum thus indicates that the Soret band excitation of $Cu^{II}TPP$ is accompanied with structural change along the Cu–N coordination axis, which suggests that the nearby charge transfer electronic state might play a role in the dephasing process in $Cu^{II}TPP$.

In summary, we report here, for the first time, the directly measured Soret band lifetimes of H_2TPP and $Cu^{II}TPP$ using the femotosecond-resolved fluorescence up-conversion technique. Although the detailed mechanism of the ultrafast electronic
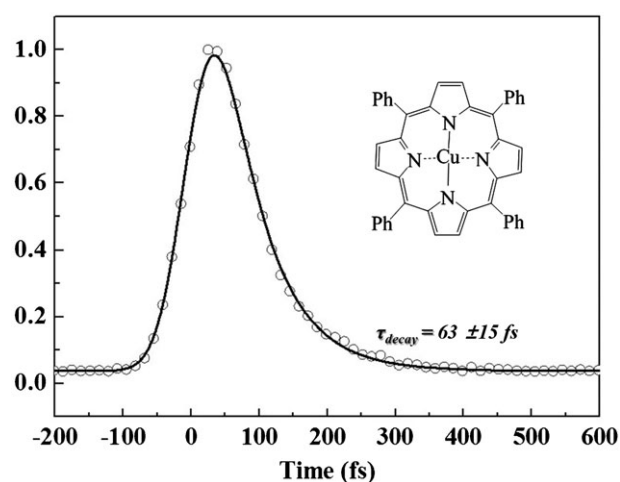

Fig. 2 Time-resolved fluorescence up-conversion transient of the Soret band of $Cu^{II}TPP$ in benzene (○). The concentration of $Cu^{II}TPP$ is 5×10^{-4} M. The solid line is the fit to the experimental data.
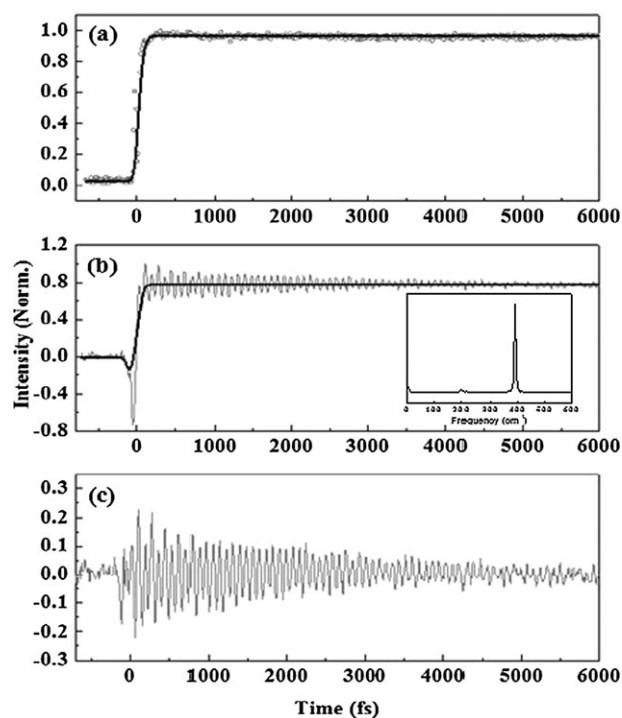

Fig. 3 Transient absorption transients of (a) H_2TPP (○), (b) $Cu^{II}TPP$ (gray solid line), and (c) residual from the subtraction of the fit from raw data in (b). Sample concentrations are 5×10^{-5} M. Black solid lines are fits to the experimental data. The Fourier transformed spectrum of $Cu^{II}TPP$ is shown in the inset in (b).

dephasing of the Soret band of the porphyrin systems is still uncertain, our experimental lifetime measurements here would stimulate the further investigation of this important subject.

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