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S_2 Fluorescence Dynamics of *meso*-Aryl-Substituted Subporphyrins**

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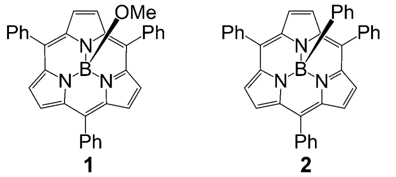
Porphyrins are one of the most intensively studied families of compounds owing to their role as key pigments in photosynthesis.[1] Nowadays, the electronic and vibrational relaxation processes that occur within porphyrins are thoroughly understood. Furthermore, it is now known that modifications of the peripheral substituents and altering the identity of the metal atom present in the central cavity have a significant impact on the photophysics of the porphyrin system. These vital pieces of information have made it possible to unravel the fundamental mechanism of photosynthesis as well as to develop applications of porphyrins across a wide range of research disciplines.

In organic photovoltaic (OPV) cells, for instance, the efficiency of the light-to-current conversion processes is limited by the amount of energy dissipated in the early stages following light absorption. The excess photon energy is usually dissipated by ultrafast internal conversion (IC) and vibrational energy redistribution.[2] Thus, a complete understanding of the dynamics of higher excited states is essential for an improvement of the performances of OPV devices. Gaining insight into the dynamics of higher excited states of molecular systems has been difficult, as time-resolved absorption spectroscopy measurements often give rise to congested spectra. On the other hand, because of a lack of spectral congestion, fluorescence spectroscopy and time-resolved fluorescence decay profiles allow the unequivocal assignment of dynamics observed for excited states. In this regard, the observation of emissions from higher excited states has offered a unique opportunity to thoroughly understand the mechanism of electronic relaxation processes. Porphyrins are amongst a few molecules that display dual fluorescence from the second excited singlet state. By virtue of porphyrin S_2 fluorescence, the dynamics of higher excited states of porphyrins, such as free-base tetraphenylporphyrin (H_2TPP), magnesium tetraphenylporphyrin (MgTPP), zinc tetraphenylporphyrin (ZnTPP), and zinc phtalocyanine tetrasulfonate ($ZnPcS_4$), have been extensively studied.[3]

In recent years, subporphyrins, which may be considered as ring-contracted porphyrin analogues because of a regular arrangement of three constitutional pyrrole rings and three carbon atoms in an alternate fashion, have emerged as a novel class of promising functional pigments.[4] Unlike for porphyrins, little is known about the photophysical behavior of subporphyrins, and until now, the observation of their S_2 fluorescence has not been reported. Thus, information regarding the higher excited states of subporphyrins is of great interest in its own right, and would lead to an in-depth understanding of the nature of the excited electronic states of subporphyrins.

Although *meso*-triaryl-substituted subporphyrins exhibit intriguing optical properties, such as nonplanar aromaticity and exceptionally strong electronic coupling with aryl substituents in the *meso* position, their orbitals have features similar to those of aromatic porphyrinoids, such as *meso*-tetraaryl-substituted porphyrins.[4b] These attractive and advantageous properties prompted us to explore the possibility of detecting the S_2 fluorescence of *meso*-triaryl-substituted subporphyrins. The main focus of this work was to explore whether S_2 fluorescence could be observed for *meso*-triaryl-substituted subporphyrins. It would also be beneficial to determine the S_2 lifetimes and to identify electronic structures of subporphyrins. Herein, we report the first unambiguous observation of S_2 fluorescence for B(methoxo)-triphenylsubporphyrin **1** and B(phenyl)-triphenylsubporphyrin **2**[5] (Scheme 1) by femtosecond time-resolved fluorescence upconversion techniques.

The absorption and fluorescence spectra of subporphyrins **1** and **2** were measured in toluene and displayed characteristic spectral features (Figure 1): an intense Soret band at 350–410 nm, Q bands at 420–550 nm (approximately one order of magnitude smaller than the Soret band), and a fluorescence profile with two peaks at 500–650 nm. The emission profiles at 500–650 nm were assigned to S_1 fluorescence of the subpor-



1 **2**

Scheme 1. Molecular structures of subporphyrins **1** and **2**.

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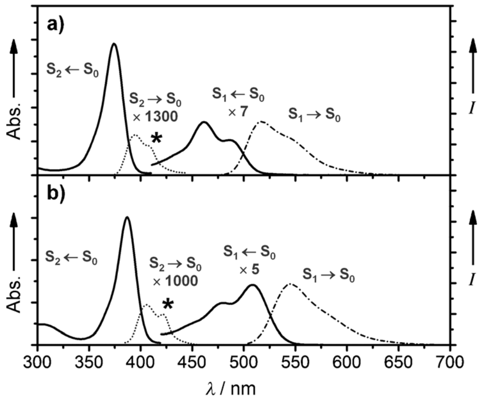

Figure 1. Ground-state absorption and static fluorescence spectra of subporphyrins **1** (a) and **2** (b) in toluene. For the fluorescence spectra, the excitation wavelengths were 370 and 375 nm, respectively. The asterisks (*) indicate Raman peaks of the solvent. —— absorption; ••••• S_2 emission; –•–• S_1 emission.

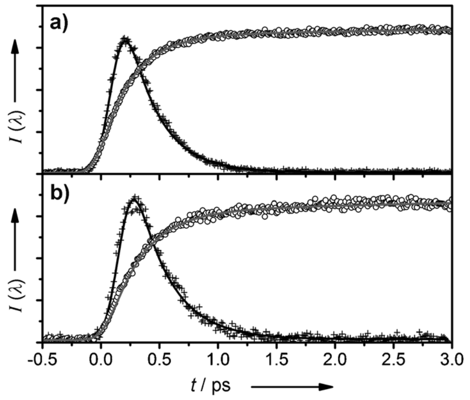

Figure 2. Time-resolved fluorescence decay profiles of **1** (a) monitored at 425 nm (B; +) and 530 nm (Q; ○), and of **2** (b) at 420 nm (B; +) and 540 nm (Q; ○) with photoexcitation at 380 nm in toluene. Solid lines (—— and ——) are fits of the experimental data.

phyrins, as they are the mirror images of the Q-like absorption bands. Compared with the corresponding four-pyrrole ring congener ZnTPP, the absorption and fluorescence spectra of the subporphyrins **1** and **2** are blue-shifted, which reflects the contracted 14 π-conjugated system. Other photophysical properties of the S_1 states of **1** and **2**, however, indicate that they feature aromatic properties that are analogous to those of ZnTPP (Supporting Information, Table S1 and Figure S1).

Importantly, a further fluorescence profile at approximately 380–450 nm was observed for **1** and **2** upon excitation at the respective Soret-like band at about 350–410 nm, which certainly differs from the S_1 fluorescence. These fluorescence spectra were assigned to be due to S_2-to-S_0 (S_2) fluorescence because they are mirror images of the S_2–S_0 absorption. According to Kasha's rule, a highly excited S_n state can emit fluorescence only for a very short period of time before electronic relaxation to the lowest S_1 state occurs; thus, the time-integrated intensity of S_n fluorescence is negligibly small compared to that of S_1 fluorescence.[6] In other words, almost all of the steady-state fluorescence spectra of molecules originate from the lowest excited singlet state (S_1), even when the molecule is initially photoexcited to the highest excited singlet state. Our observation of the dual fluorescence for **1** and **2** indicates that these molecules do not obey Kasha's rule. This can be attributed to a large energy gap between the S_1 and S_2 states of subporphyrins. In general, radiationless IC is governed by the energy-gap law.[3c,7] A large energy gap usually leads to a decrease in the IC rate owing to a poor Franck–Condon factor. Thus, as for ZnTPP (6660 cm^{-1}), the large S_2–S_1 energy gaps of **1** and **2** (6200 and 6170 cm^{-1}, respectively) could lead to a violation of Kasha's rule and allow the detection of S_2 fluorescence.

To explore the intrinsic excited-state relaxation dynamics of subporphyrins **1** and **2**, fluorescence transients were recorded with our fluorescence upconversion apparatus. The time-dependent profiles of the S_2 and S_1 fluorescence of subporphyrins in toluene are shown in Figure 2. The S_2 fluorescence decay profile of **1** at 425 nm is well-described by a single-exponential decay model with a time constant of 280 fs, whereas the S_1 fluorescence profile at 530 nm exhibits a rise with two distinct time constants of 270 fs and 5.3 ps, and then decays on a nanosecond time scale. Similarly, the S_2 fluorescence decay profile of **2** is well-described by a single-exponential decay model with a lifetime of 290 fs, whereas the time-dependent S_1 fluorescence profile shows a rise with time constants of 310 fs and 4.5 ps and a single decay on the nanosecond time scale. As the decay component of S_2 fluorescence and the rise component of S_1 fluorescence are almost identical, these time constants can be assigned to the IC process from the S_2 to the S_1 state. According to several literature precedents,[3c,7a] the components of a picosecond time scale likely represent vibrational relaxation accompanied by solvation processes. Interestingly, we found that the S_2–S_1 IC rates of **1** and **2** are significantly shorter than that of ZnTPP. The fluorescence decay profile of ZnTPP shows a single decay component of 1.60 ps at 440 nm (S_2 fluorescence), which is in good agreement with previously reported values. Therefore, we could deduce that the S_2–S_1 IC rates of these subporphyrins are approximately five times greater than that of ZnTPP (Table 1).

In time-dependent perturbation theory, the rate of irreversible radiationless relaxation strongly correlates with the inter-state coupling energy and the density-of-state-weighted Franck–Condon factor.[3a,8] According to this expression, which is known as Fermi's golden rule, a greater Franck–Condon factor should accelerate the radiationless decay. This can invoke a significant acceleration of the S_2–S_1 IC processes of subporphyrins **1** and **2**, as broader Q bands

Table 1: Best-fit parameters of the femtosecond fluorescence upconversion transients of **1** and **2** in toluene.

Compound	B (S_2)		Q (S_1)	
	τ_{S2} [ps]	$\tau_{S1,1}$ [ps]	$\tau_{S1,2}$ [ps]	$\tau_{S1,3}$[a] [ps]
1	0.28	0.27 (39%)	5.30 (26%)	2.8 (35%)
2	0.29	0.31 (47%)	4.47 (6%)	2.4 (47%)

[a] The third time constants were fixed by the values from time-correlated single photon counting (TCSPC) data. The values in brackets denote the relative amplitude of each time constant.

were observed in the absorption spectra of **1** and **2** than in those of ZnTPP. The spectral difference in the Q bands is thought to originate from structural differences between a subporphyrin and ZnTPP (domed and planar structures, respectively).[4a,c,9] Therefore, we conclude that these distinct structural features of the subporphyrin increase the density of the vibronic states, which may play an important role in shortening the lifetime of the excited S_2 states of all subporphyrins relative to ZnTPP.

To investigate the nature of the electronic excited states of subporphyrins, we have measured the fluorescence anisotropy decay profile of **2** by femtosecond fluorescence upconversion techniques. Unfortunately, we could not clearly measure the fluorescence anisotropy decay profile of **1** because of very weak emission from the S_2 state. The fluorescence anisotropy profile for the S_2 state of **2** decays from $r_0 = 0.32$ to $r_{\text{inf}} = 0.1$ and is composed of an anisotropy time constant of 170 fs (Figure 3). As described by Wynne, Hochstrasser, and co-workers[3d,10] for a degenerate system with mutually orthogonal transition dipole moments, the anisotropy shows an initial value of 0.7. This value then decays to 0.4, mainly as a result of electronic dephasing. When the two states are completely dephased with equal populations, the anisotropy reaches a value of 0.1 by intramolecular energy equilibration between the degenerate states. Thus, the observed time constant for the anisotropy decay of **2** could be due to a partial dephasing process between the degenerate states as well as to equalization of the population. The time constant of 170 fs is slightly larger than that for ZnTPP (ca. 130 fs; Figure S2). Presumably, the relatively weak oscillator strengths of the B states of **2** lead to slow dephasing and a long population equilibrium time. The anisotropy value of **2** remains at approximately 0.1, although a low initial anisotropy value of 0.32 was observed as compared to $r_0 = 0.7$ because of the relatively broad instrument response function (180 fs) of our upconversion apparatus. The anisotropy value of 0.1 for metalloporphyrins at longer times is explained by the existence of orthogonal transition dipole moments of degenerate S_2 states as a result of D_{4h} symmetry. Hence, in the case of subporphyrins with C_3 symmetry, the anisotropy values should be higher than 0.1. However, the fact that the anisotropy of subporphyrin decays to 0.1 indicates that, despite its C_3 symmetry, the transition dipole moments of the two B band transitions of subporphyrins are oriented orthogonally. Consequently, we can deduce that differences in symmetry or structure between porphyrins and subporphyrins, which alter IC rates and anisotropy decay rates, do not have a significant effect on the relative orientation of the transition dipole moments.

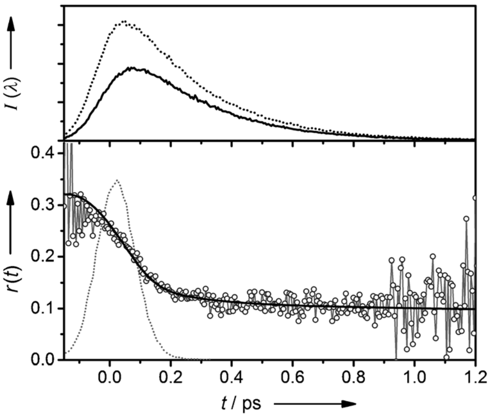

Figure 3. Time-resolved fluorescence (top) and anisotropy (bottom; ○) decay profiles of the B state of **2** in toluene obtained by fluorescence upconversion monitored at 420 nm, with photoexcitation at 385 nm. vv (•••••) and vh (——) indicate the fluorescence decay when the excitation light is vertically polarized, and only the vertically or horizontally polarized portions of fluorescence are detected. The solid line (——; bottom) is a fit of the experimental data.

We have demonstrated the first direct observation of S_2 fluorescence of subporphyrins. Simultaneous monitoring of the decay and rise of S_2 and S_1 fluorescence allowed us to reveal the S_2 deactivation and S_1 population dynamics of subporphyrins. Furthermore, based on our observation of the anisotropy in the higher excited states of subporphyrins, it may be deduced that the two transition dipole moments of degenerate S_2 states are orthogonally oriented despite the C_3 symmetry of the molecules. Hence, we believe that this report has successfully identified fundamental photophysical properties and relaxation dynamics of higher excited states of subporphyrins. As subporphyrins have recently emerged as a new class of functional macrocycles,[4e] particularly in view of their highly tunable electronic and optical properties, information regarding the excited-state dynamics of subporphyrins is of high importance. Therefore, we think that these findings not only give an insight into future experimental and theoretical studies of subporphyrins, but also pave the way for the use of subporphyrinoid systems as molecular materials.

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