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From chlorophyll a towards bacteriochlorophyll a: excited-state processes of modified pigments

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Abstract

By means of fluorescence spectroscopy and nonlinear absorption experiments, excited-state processes of the modified pigments [3-acetyl]-chlorophyll a, [3¹-OH]-bacteriochlorophyll a and [3-vinyl]-bacteriochlorophyll a were investigated and compared with those of chlorophyll a and bacteriochlorophyll a.

1. Introduction

Excited-state properties of pigments of higher plant and bacterial photosynthesis and of related modified pigments are of multifarious interest, e.g., as basic information for molecular (excited-state) engineering, also with respect to the photophysical processes of photosynthesis and their alteration in case of pigment exchange, as well as with respect to photochemistry in view of photodynamic therapy. Some were published recently, especially those of chlorophyll a, bacteriochlorophyll a, chlorophyll b and 20-chloro-chlorophyll a [1,2]. For a more detailed characterization of the effect of the transit chlorophyll a (Chla) → bacteriochlorophyll a (BChla) on the excited state properties, further fluorescence spectroscopy and nonlinear absorption studies were carried out with the modified pigments [3-acetyl]-Chla and [3-vinyl]-BChla.

because the structural differences between Chla and BChla involve the degree of unsaturation (chlorin versus bacteriochlorin) as well as a changed substituent at C-3 (vinyl versus acetyl), these modified pigments characterize two ways of this transit. Also investigated was the [3¹-OH]-BChla, in which the C-3 substituent has no double bonds capable of conjugation with the macrocycle.

2. Experimental

The pigments investigated were prepared as described in [3]. The solvent diethylether was of UVASOL grade. Fluorescence spectra, emission cross-sections, quantum yields, decay times and ISC rates were determined according to Ref. [4] and literature cited therein. For determination of the fluorescence quantum yields of [3-vinyl]-BChla and [3¹-OH]-BChla, the reference compound was BChla ($\phi_F = 0.19$, [5]), whereas the quantum yield of [3-acetyl]-Chla was calibrated against Chla ($\phi_F = 0.32$, [1]). The nonlinear absorption apparatus and the data processing were described in

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Ref [6]. Excitation was performed by a dye laser pumped by a nitrogen laser (pulse duration: 1.4 ns, pulse energy: 6–12 μJ). For further details cf. [1].

3. Results and discussion

3.1. Fluorescence, internal conversion and intersystem crossing

In Table 1 the excited state deactivation parameters are summarized. The radiative lifetime ($1/k_R$) of all pigments investigated is approximately the same. The differences in the fluorescence lifetime (τ) are mainly caused by intersystem crossing (ISC). Change to a C7–C8 single bond gives increased ISC in both cases (Chla \rightarrow [3-vinyl]-BChla; [3-acetyl]-Chla \rightarrow BChla), whereas in cases of a vinyl \rightarrow acetyl transition the ISC change within the same macrocycle conjugation system is minor. Our results for BChla differ from that of Connolly et al. [5], who discussed smaller ISC yields ($\phi_{isc} \approx 0.4$) obtained from theoretical calculations, and correlate with earlier experimental results of Gurinovich et al. [7]. The rate constants for internal conversion (k_{ic}) are about one order of magnitude lower than for intersystem crossing and do not differ markedly. An exception is [3¹-OH]-BChla where k_{ic} is en-

larged by a factor of about two. Probably, this could be explained by the loss of conjugation of the C-3 substituent with the macrocycle leading to an additional energy dissipation by the rotation of this group.

3.2. Excited-state absorptions

The values for the excited-singlet-state absorption cross-sections (cf. bar graphs in Figs. 1 and 2) were calculated by curve simulation of intensity-dependent transmission curves measured for distinct excitation wavelengths. For this an energy level scheme with two absorption steps in the singlet and one in the triplet system (cf. inset of Fig. 1) was utilized considering the rate constants of Table 1. The Franck–Condon relaxation (FC) and the triplet parameters were generally set to $k_{FC} = 1 \times 10^{12} \text{ s}^{-1}$, $k_{ph} = 1 \times 10^4 \text{ s}^{-1}$, $\sigma_T < 5 \times 10^{-17} \text{ cm}^2$, $k_{Tn} = 1 \times 10^{12} \text{ s}^{-1}$. Furthermore, it proves necessary to consider the cross-sections for stimulated emission σ_{em} at least for the long-wavelength side of the S₁ absorption band ($\lambda(\text{nm})/\sigma_{em} \times 10^{16} (\text{cm}^2)$): Chla – 666/2.6, 669/2.5; [3-acetyl]-Chla – 677/2.3, 686/3.4; [3¹-OH]-BChla – 730/2.3, 734/3, 738/3.3, 740/3.3; [3-vinyl]-BChla – 750/2.5, 755/2.9, 760/3, 770/2.2; BChla – 775/3.8, 780/4.3, 785/4.4, 790/3.6).

Table 1
Excited-state deactivation channels of Chla, [3-acetyl]-Chla, [3¹-OH]-BChla, [3-vinyl]-BChla and BChla in diethylether

Compound	τ (ns)	ϕ_F	ϕ_{isc}	ϕ_{ic}	τ_{s_x} (ps)
		$k_R (\text{s}^{-1})$	$k_{isc} (\text{s}^{-1})$	$k_{ic} (\text{s}^{-1})$	
Chla	6.0 ± 0.2	0.32 5.310^7	0.60 110^8	0.08 1.310^7	≈ 5
[3-acetyl]-Chla	5.9 ± 0.2	0.41 6.910^7	0.49 8.310^7	0.10 1.710^7	≈ 50
[3 ¹ -OH]-BChla	2.9 ± 0.2	0.23 710^7	0.67 210^8	0.10 3.410^7	≈ 50
[3-vinyl]-BChla	3.1 ± 0.2	0.20 6.510^7	0.75 2.410^8	0.05 1.610^7	≈ 5
BChla	3.0 ± 0.2	0.19 6.310^7	0.76 2.510^8	0.05 1.710^7	≈ 10

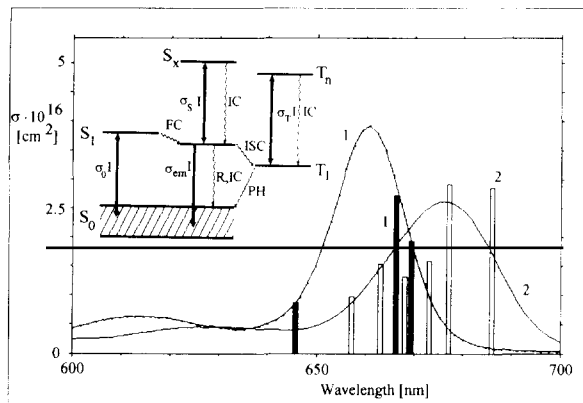


Fig. 1. Cross-sections of the excited singlet absorption σ_s (bar graph) in comparison to the ground-state absorption cross-sections σ_o (curves) for (1) Chla and (2) [3-acetyl]-Chla in diethylether at room temperature; Chla: $c = 1 \times 10^{-6}$ M, [3-acetyl]-Chla: $c = 2.5 \times 10^{-6}$ M; inset: energy level scheme for simulation of nonlinear absorption curves (cf. text).

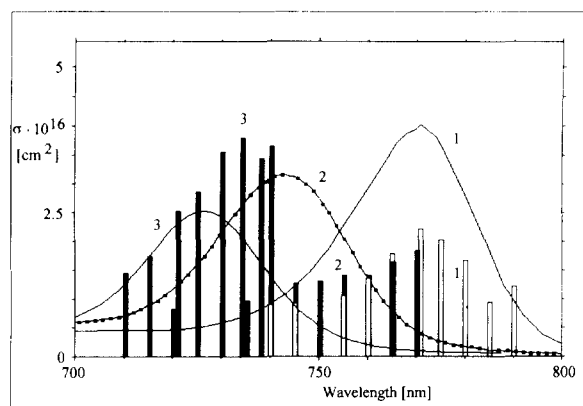


Fig. 2. Cross-sections of the excited singlet absorption σ_s (bar graph) in comparison to the ground-state absorption cross-sections σ_o (curves) for (1) BChla, (2) [3-vinyl]-BChla and (3) [3¹-OH]-BChla in diethylether at room temperature; BChla: $c = 4.4 \times 10^{-6}$ M, [3-vinyl]-BChla: $c = 2.9 \times 10^{-6}$ M, [3¹-OH]-BChla: $c = 2.6 \times 10^{-6}$ M.

Strong excited-state absorptions in the region of the ground-state absorption band could be found for all pigments investigated (cf. Figs. 1 and 2). The

calculated values for the relaxation of the S_x level (τ_{S_x}) are included in Table 1.

4. Conclusions

The radiative lifetimes for the series Chla \rightarrow [3-acetyl]-Chla \rightarrow [3¹-OH]-BChla \rightarrow [3-vinyl]-BChla \rightarrow BChla are almost equal. However, the fluorescence lifetimes decrease in this order and the differences are mainly related to the presence or absence of a fully unsaturated ring B. With exception of [3-acetyl]-Chla this correlates with increased ISC. For all compounds strong excited-state absorptions within the $S_0 \rightarrow S_1$ absorption band were found.

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