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Photophysical properties of gallium hydroxyl tetratolylporphyrin and 13^2-demethoxycarbonyl-(gallium hydroxyl)–methyl-pheophorbide *a*

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Abstract

Two metal tetrapyrroles containing gallium, gallium hydroxyl tetratolylporphyrin and 13^2-demethoxycarbonyl-(gallium hydroxyl)–methyl pheophorbide *a* (Ga-(OH)-chlorin), were synthesized from their respective free bases using Ga(III)-acetylacetonate in a phenol melt. Their photophysical properties were investigated and the quantum yields of different monomolecular deactivation processes were determined. For Ga-(OH)-porphyrin S_2-fluorescence was observed and quantified. In contrast, for Ga-(OH)-chlorin no S_2-fluorescence was observed. Both compounds should be useful as efficient photosensitizers in photodynamic therapy.

1. Introduction

Metal porphyrin derivatives are biologically important chromophores with a macrocyclic-conjugated system of π-electrons. The synthesis and photophysical characterization of metal porphyrins and especially the diamagnetic Ga-porphyrin-complexes were and still are a hot topic in chemistry and optical spectroscopy [1–4]. Characteristic and partly intense B and Q absorption bands in the near-ultraviolet and visible regions, respectively, arise from the $(\pi \rightarrow \pi^*)$ transitions of the electronic system of the porphyrin. In case of closed shell configuration of the central metal, the outer-shell electrons give only a minor perturbation [3,5].

Specifically, several reports on Ga-porphyrin-complexes have appeared in the past, where both synthetic procedures and photophysical studies were in the center of interest [1–4]. Insertion of gallium into porphyrins has been achieved by two different synthetic approaches in the past: reaction of the free base with gallium (III)-salts, e.g. chloride, in acetic acid [6] and by the solvent-free procedure by reacting the porphyrin with gallium (III)-acetylacetonate in a phenol melt [7].

Interestingly, no photophysical studies on gallium chlorins have been published to our knowledge, and preparative chemistry is largely unknown. Generally, synthetic procedures and photophysical properties of free base chlorins and of a large variety of metal chlorins, especially chlorophyll *a* derivatives, have been studied extensively for decades [8–15]. Related gallium containing species, however, do not seem to have gained much interest, even though the additionally available axial position in gallium centered tetrapyrroles could be particularly useful as a versatile coupling site for the synthesis of novel donor–acceptor systems. Such novel dyads could be utilized in the investigation of photoinduced energy or electron transfer.

Moreover, on the way towards 2nd and 3rd generation photosensitizers for photodynamic therapy (PDT) [16], besides a number of porphyrins, certain chlorins were considered as prospective photosensitizing molecules [17]. Their characteristic absorption spectra with bands in the far red spectral region with large extinction coefficients combined with high quantum yields for singlet oxygen generation [18] suggest their potential efficiency in photodynamic activity.

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In 1971, Bajema et al. [19] first observed S_2-fluorescence of a porphyrin: zinc tetrabenzoporphyrin (zinc tetraphenylporphyrin) in octane and in argon matrices. Since that time emission from higher excited states was observed for a variety of diamagnetic metal porphyrins [3,5,19–24]. The large energy gap (Ga-(OH)-TTP: 6800 cm^{-1}) and the parallel energy surfaces of S_1 and S_2 state retard the internal conversion between the two states. Therefore a greater transition moment granted to $S_2 \rightarrow S_0$ transition yields emission from the S_2 state [5]. Ohno et al. investigated the S_2-fluorescence of different metal porphyrins and also for a gallium porphyrin (Ga-Cl-TPP in benzene) [3].

The steady state S_2-fluorescence can be used as a reference to determine the rates of photoinduced electron transfer (PET) in, e.g., thin layers like Langmuir–Blodgett-films, where the fluorescence intensity is very low and time resolved measurements become impossible. Due to the fact that only the S_1 contributes to the PET, the ratio between the intensities of S_1- and S_2-fluorescence can be considered as measure of PET rates [25].

In a comparative study we investigated the photophysical properties of Ga-(OH)-TTP and a novel semi synthetic Ga-(OH)-chlorin derived from chlorophyll *a*, and evaluated their suitability as either electron donor in electron transfer systems or as efficient photosensitizer for PDT. This study is expected to re-focus attention on gallium containing tetrapyrroles and to stimulate further preparative-synthetic and photophysical investigations.

2. Materials and methods

2.1. Sample preparation and analysis

Tetratolylporphyrin, gallium acetylacetonate, phenol and common laboratory solvents were obtained from Sigma–Aldrich, Taufkirchen, Germany. 13^2-Demethoxycarbonyl methylpheophorbide *a* was obtained by extracting and processing the blue–green algae *Spirulina maxima* following a procedure of Smith et al. [26]. NMR-spectra were recorded using a Bruker DRX-300 NMR spectrometer (300 MHz for ^1H). Mass analysis was performed with a Finnigan MAT 90 spectrometer and UV/VIS spectra were recorded on a Shimadzu 160A spectrometer.

Tetratolylporphyrin-hydroxy-gallium (III)-complex ***(1)*** was synthesized according to the literature procedure by Buchler and Puppe [7], starting from the TPP free base, phenol and gallium (III)-acetylacetonate. The NMR and mass spectroscopic data are in accordance with the literature reports of the first published synthesis of this compound by Eaton et al.[6].

13^2-*Demethoxycarbonyl methylpheophorbide a–hydroxy-gallium (III)-complex* ***(2)***. In modification of the above procedure, 300 mg (0.35 mmol) 13^2-demethoxycarbonyl methylpheophorbide *a*, 125 mg (0.35 mmol) Ga(III)-acetylacetonate and 1 g phenol in a 10 ml flask under argon and heated for 15 min at 140 °C on a metal bath. Subsequently the excess phenol was removed by Kugelrohr distillation under reduced pressure. The crude reaction mixture was subjected to flash chromatography on silica to hydrolyze the phenoxide, using THF/MeOH (9:1) as eluent. The major blue–green band was collected and purified by chromatography on neutral aluminium oxide, eluting with chloroform to give 110 mg (35%) as a blue–green solid.

^1H NMR (300 MHz, $CDCl_3$): 9.14 (s, 1H, 10-H), 9.01 (s, 1H, 5-H), 8.39 (s, 1H, 20-H), 7.88 (dd, $J_{3\text{-}1,3\text{-}2A} = 17.7$ Hz, $J_{3\text{-}1,3\text{-}2B} = 11.3$ Hz, 1H, 3^1-H), 6.14 (dd, $J_{3\text{-}2A,3\text{-}2B} = 1.7$ Hz, $J_{3\text{-}2A,3\text{-}1} = 17.8$ Hz, 1H, 3^{2A}-H), 6.04 (dd, $J_{3\text{-}2B,3\text{-}2A} = 1.7$ Hz, $J_{3\text{-}2B,3\text{-}1} = 11.5$ Hz, 1H, 3^{2B}-H), 4.82 (2d, $J = 19.7$ Hz, 2H, 13^2-CH_2), 4.40 (m, $J_{17,18} = 1.9$ Hz, $J_{18,18Me} = 7.1$ Hz, 1H, 18-H), 4.15 (m, 1H, 17-H), 3.48 (q, $J = 7.6$ Hz, 2H, 8^2-CH_2), 3.32 (s, 3H), 3.03 (t, $J = 6.3$ Hz, 2H, 17^2-CH_2), 3.31 (s, 3H), 3.22 (s, 3H), 2.52 (m, 1H, 17^{1A}-H), 2.21 (m, 1H, 17^{1B}-H), 1.83 (d, $J = 7.2$ Hz, 3H, 18-Me), 1.55 (t, $J = 7.6$ Hz, 3H, 8^1-Me), 1.43 (m, 1H, 17^{2A}-H), 1.25 (m, 1H, 17^{2B}-H).

EI-MS: *m*/*e*: ber. für $C_{34}H_{35}GaN_4O_4$: 633,4, gef.: 633,2 (10%, M^+), 616 (60%, M–OH).

2.2. Steady state absorption and fluorescence

Ground state absorption spectra were recorded at room temperature using the commercial spectrophotometer Shimadzu UV160A. The emission spectra of the compounds dissolved in toluene were taken at room temperature in a 1 cm × 1 cm optical quartz cell using a Ti:Sapphire-laser (Mira 900, Coherent) for excitation at 400 nm and a polychromator with a CCD matrix for detection (LOT-Oriel, Instaspec IV). As reference for measurements of fluorescence quantum yield free base tetraphenylporphyrin (H_2TPP) in toluene ($\phi_{fl} = 0.11$) [27] was used.

2.3. Time resolved fluorescence

Time resolved fluorescence measurements of the samples dissolved in toluene were carried out by time-correlated-single-photon-counting-technique (Becker & Hickl GmbH, SPC 300) using frequency-doubled pulses of a Ti:Sapphire-Laser (Coherent Mira 900, 350–460 nm, FWHM 120 fs) for excitation. The response function of the system, measured with a fiber as scatter medium, had a FWHM of about 60 ps. The setup was previously described in [28].

2.4. Singlet oxygen generation

Photosensitized generated singlet oxygen luminescence (SOLM) of the molecules dissolved in toluene was measured time resolved at 1270 nm. A nanosecond Nd–YAG laser (BMI) together with an OPO (BMI) was used to excite the samples at 510 nm. The luminescence signal was recorded using a germanium pin diode (Northcoast). For calculation of the singlet oxygen quantum yield of both samples H_2TPP in toluene was used as reference ($\phi_\Delta = 0.68$) [18]. The setup and details are described elsewhere [29].