



Metallo complexes of *meso*-phenothiazinylporphyrins: Synthesis, linear and nonlinear optical properties



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ABSTRACT

Herein we described the synthesis and the structural characterization of series of metallo-*meso*-(phenothiazin-3yl)porphyrins containing Ni(II), Cu(II), Zn(II) or Pd(II) coordinated in the central cavity of the macrocycle and an increasing number of peripheral phenothiazine units (from one up to four). Their photophysical properties including UV–vis linear (one photon) and nonlinear (two photons) absorption and fluorescence emissions were investigated in solution or solid state. Fluorescence lifetimes of the new metallo-phenothiazinylporphyrins in the solid state were measured using a time correlated single-photon counting method. Nonlinear optical properties were observed using a Titanium: Sapphire femtosecond laser. Two-photon excited fluorescence emissions of red light for selected Zn(II)-, Cu(II)- and Pd(II)-*meso*-phenothiazinylporphyrins, as well as second harmonic generation in the case of some Cu(II)- and Pd(II)-*meso*-phenothiazinylporphyrins are reported.

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1. Introduction

Nonlinear optical (NLO) materials capable of producing modified electromagnetic fields that are different from the input field in phase, frequency or amplitude have attracted an increasing interest lately due to their potential applications in optical information storage, optical logic gates, laser radiation protection and phase locked laser mode. Second harmonic generation (SHG) is a nonlinear optical process responsible for doubling the frequency of an input optical wave, commonly used to produce green light (532 nm) from a Nd:YAG laser operating at a wavelength situated in the NIR region (1064 nm).

Organic materials capable of producing optical nonlinearities represent an active field of research at the interface of modern physics, chemistry and materials science [1]. The design and synthesis of new multiphoton active chromophores with special tailored properties have strong roots in both fundamental research and applications of multiphoton absorption, multiphoton excitation and multiphoton active materials [2]. Second harmonic generation (SHG) properties of suitable candidates for applications in both imaging and signal processing were correlated with structural characteristics such

as asymmetry of the molecular structure, prominent delocalization of π -electrons systems and large hyperpolarizability [3].

The structure–photophysical properties relationships of porphyrin based absorbing chromophores were assigned by means of both experimental evidence and theoretical calculations after modulating the nature and position of the substituents, the linker conjugation and metal insertion. Large excited-state absorption and long triplet lifetime were reported for asymmetrically substituted porphyrins [4]. Electron rich heteroaromatic units such as carbazole [5] or thiophene [6], as well as electron deficient heterocycles such as pyrimidine [7] or pyridine [8] respectively, were employed in the peripheral functionalization of the porphyrin macrocycle and in each case different metal cations were coordinated into the central cavity of *meso* functionalized porphyrin free bases using reported procedures which afforded metalated porphyrins in moderate to good yields [9].

Various strategies for increasing the overall efficiency of the two-photon absorption processes in porphyrin related molecular systems were reviewed pointing towards key factors such as charge transfer character, unidirectional elongation of π -conjugation, as well as efficient π -conjugation pathways throughout the whole molecular framework [10]. Several ethynylene and vinylene linked porphyrin dimers and porphyrin oligomers were reported and their

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structure—two photon absorption (2PA) property relationships were discussed [11].

SHG signals generated by porphyrin derivatives were observed [12] and a significant enhancement of hyperpolarizability was achieved through metal insertion at the ring center, or by functionalization at the peripheral positions [13].

Continuing our investigations regarding the properties of *meso*-phenothiazinylporphyrins (MPP) containing a variable number of peripheral phenothiazine and phenyl units [14], we report here the preparation of their metallo-complexes with selected d-block elements possessing polarizable valence electrons capable of perturbing the π -electron system of the porphyrin core and thus inducing a modification of the non-linear optical response of the assembly. We examined the effect of metal substitution on the UV–vis linear and nonlinear optical response using combined experimental and computational methods. The fluorescence emission upon one or two photon absorption in the solid state and second harmonic signal generation reported here are, to the best of our knowledge, the first case of phenothiazine functionalized porphyrin metallo-complexes pointing towards suitable properties for optical device applications.

2. Materials and methods

2.1. Spectral measurements

The mass spectra were recorded on an HRMS spectrometer LTQ Orbitrap XL-Thermo-Scientific using APCI or ESI ionization technique.

NMR spectra were recorded at room temperature on Bruker Avance instruments ($^1\text{H}/^{13}\text{C}$: 400 MHz/100 MHz or 300 MHz/75 MHz) in solution (deuteriated solvents chloroform (CDCl_3), or DMSO).

UV–vis spectra were recorded in CH_2Cl_2 with a Perkin Elmer Lambda 35 spectrophotometer.

Fluorescence spectra in solution were recorded in CH_2Cl_2 with a Perkin Elmer PL 55 spectrophotometer. The fluorescence quantum yield was calculated using tetraphenylporphyrin (TPP) standard $\Phi = 0.13\%$ in DCM solution [15].

Fluorescence and second harmonic generation (SHG) measurements on solid samples were performed on a MicroTime 200 time-resolved confocal fluorescence microscope system (PicoQuant) coupled with an SR-163 spectrograph, covering a window of 260 nm, equipped with a Newton 970 EMCCD camera (Andor Technology) and a tunable Coherent Mira 900 Titanium: Sapphire femtosecond laser, using a $60\times/\text{NA} = 1.2$ magnification water objective. One-photon excited fluorescence emission (1PE) measurements were carried out using a 0.4 μW picosecond diode laser head operating at 405 nm/40 MHz (LDH-D-C-405, Pico-Quant) as excitation source. The signal was collected through the objective and was spatially and spectrally filtered by a 50 μm pinhole and an HQ430LP (Chroma, USA) emission filter. For time-resolved measurements, the filtered signal was focused on a PDM Single Photon Avalanche Diode (SPAD) from MPD. The detector signals were processed by the PicoHarp 300 Time-Correlated Single Photon Counting (TCSPC) data acquisition unit. Two-photon excited fluorescence emission (TPE) was investigated under excitation with 810 nm (10 mW) laser beam provided by the above mentioned Ti:Sa laser. Both 1PE and TPE spectra were recorded from different spots in the solid sample deposited on microscope cover glass (each spectrum averaged from 5 spectra taken in the same spot, 2 s integration time/spectrum). SHG was investigated under excitation between 780 and 840 nm (10 mW) using the same configuration as for two-photon excited fluorescence measurements. SHG spectra were recorded from different spots in the solid sample deposited on microscope cover glass (each spectrum averaged from 5 spectra taken in the same spot, 5 s integration time/spectrum). Both TPE and SHG signals were filtered using an FF01-750SP (Semrock, USA) emission filter.

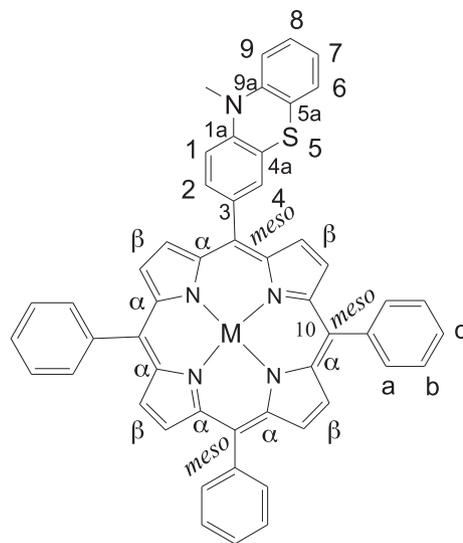
2.2. Synthesis of metallocomplexes of meso-phenothiazinylporphyrins (metallo-MPP)

Asymmetrical metallo-complexes of AB_3 type MPP containing one peripheral phenothiazine unit **1–4** and **1a–4a** (Scheme 1), metallo-complexes of $\text{trans-A}_2\text{B}_2$ type MPP containing two peripheral phenothiazine units **5–8** (Scheme 2) and metallo-complexes of A_4 type MPP containing four peripheral phenothiazine units **9–12** (Scheme 3) respectively, were obtained by incorporation of Ni(II), Cu(II), Zn(II) and Pd(II) metal ions respectively into the central cavity of the corresponding free bases MPP containing a variable number of phenothiazine units. MPP free bases were prepared according to our previously reported procedure [14] and the removal of their inner-core nitrogen protons was accomplished upon treatment with the appropriate metal(II) acetate in *N,N*-dimethylformamide (DMF) solution [9].

The structures of the synthesized metallo-MPP were confirmed by accurate mass measurements based on HRMS (some illustrative HRMS spectra are presented in Supplementary data Figs. S1 and S2). The formation of Zn(II)-MPP **1**, **1a**, **5**, Pd(II)-MPP **2**, **2a** and Ni(II)-MPP **3**, **3a**, **7** was easily confirmed in ^1H NMR analysis by the disappearance of the key signals due to inner-core NH protons of the free MPP base occurring at negative chemical shifts situated around -2.7 ppm (Illustrative 1D and 2D-NMR spectra in Supplementary data Figs. S1–S5). The paramagnetic Cu(II)-MPP complexes **4**, **4a**, **8**, **12** could not be characterized by ^1H NMR spectroscopy due to line broadening induced by the electric quadrupole moment of copper nucleus.

2.2.1. General procedure for metal insertion

Solutions of the free base porphyrin MPP (1 mmol) in DMF (10 mL) and the corresponding bivalent metal (Zn, Ni, Pd, Cu) acetate hydrate (1 mmol) in DMF (10 mL) were heated at 110°C for about 3 h (as monitored by TLC analysis using Merck pre-coated silica gel 60 F254 aluminum sheets). Upon completion of the reaction, water (50 mL) was added to the reaction mixture and the precipitate was filtered off and thoroughly washed with water and finally with methanol. In the case of compounds **9–12** the crude precipitate was supplementary washed with DMSO. The solid was purified by flash column chromatography (on silica with particle size 0.063–0.2 mm) using DCM/hexane 2/1 v/v as eluant to give the final product.



Atoms labeling for NMR assignments

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